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THE REACTION OF TETRAHYDROPYRAN WITH PRIMARY AROMATIC AMINES OVER ACTIVATED ALUMINA[1]

BY A. N. BOURNS, H. W. EMBLETON,[2] AND MARY K. HANSULD[3]

ABSTRACT

The vapor-phase reaction over activated alumina of tetrahydropyran with aniline and the toluidines has been investigated. Under optimum conditions, N-arylpiperidines were obtained in over 90% yield from aniline, *m*-toluidine, and *p*-toluidine. The cyclic ether and *o*-toluidine gave N-*o*-tolylpiperidine in a maximum yield of 66%. N-Phenylpyrrolidine was obtained in 88% yield from tetrahydrofuran and aniline as compared to 45.5% previously reported by Yur'ev.

During the past 15 years, Yur'ev and his coworkers have carried out an extensive investigation of the reaction of oxygen heterocyclic compounds, in particular, furan, tetrahydrofuran, and their methyl homologues, with ammonia and with amines over activated alumina. It was found, in general, that furan could be converted to pyrrole and to N-alkyl- and N-arylpyrroles in 20-30% yield, while tetrahydrofuran gave the corresponding pyrrolidines in 40-60% yield. Reaction temperatures, for the most part, were 400°C. or higher. Under these conditions, tetrahydrofuran with aniline, *o*- and *p*-toluidine gave, respectively, N-phenylpyrrolidine, N-*o*-tolylpyrrolidine, and N-*p*-tolylpyrrolidine in 45.5, 43.4, and 52.7% yield (4). Yur'ev (5) has also studied the reaction of tetrahydropyran with ammonia and ethylamine, obtaining piperidine and N-ethylpiperidine in 20 and 17% yield, respectively.

The investigation reported in this paper has been concerned primarily with a study of the reaction of tetrahydropyran with aniline and the three toluidines over Alcoa Activated Alumina. It was prompted by the recent availability of tetrahydropyran as a commercial chemical and by the excellent results of Evans and Bourns (1) in their recent investigation of the reaction of aniline with dimethyl ether over the Alcoa catalyst. These workers demonstrated that dimethylaniline of 99% purity is produced in nearly quantitative yield at temperatures as low as 275°C.

The reaction conditions of the initial experiment with tetrahydropyran and aniline corresponded to that reported by Yur'ev (4) in his study of the reaction of tetrahydrofuran with this amine, namely, a catalyst temperature of 400°C. and an ether–aniline molar ratio of 1:2. The expected product, N-phenylpiperidine, was formed in 45% yield which compared with the yield of N-

[1] *Manuscript received August 9, 1951.*
Contribution from the Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ont. Presented in part to Section III, Royal Society of Canada, Halifax Conference, June 1949.
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phenylpyrrolidine obtained by Yur'ev from tetrahydrofuran. It was noted, however, that the product contained no unreacted tetrahydropyran and that a considerable amount of high-boiling material and tarry residue was formed. At the same time, gaseous products were produced in an appreciable quantity, suggesting that the conditions of the reaction had been too severe. This led to a careful investigation of the influence of temperature, ratio of the reactants, and feed-rate on the yield of N-phenylpiperidine. It was found that the desired product could be obtained in a yield of 92% (based on the total ether charged) under the optimum conditions of 300°C., an ether–aniline molar ratio of 1:2, and a feed-rate of 0.321 moles of mixed reactants per 100 ml. of catalyst per hour. Comparable yields of the N-tolylpiperidines were obtained from the reaction of *m*- and *p*-toluidine with tetrahydropyran, the optimum temperature in this case being 325°C. With *o*-toluidine, on the other hand, the yield of the expected product, N-*o*-tolylpiperidine, was markedly lower and a relatively large high-boiling fraction was obtained. At 300°C., the yield was only 45%, while the maximum yield of 66% was obtained at 340°C.

Of the three N-tolylpiperidines, only the ortho compound appears not to have been reported previously in the literature. N-*p*-Tolylpiperidine and N-*m*-tolylpiperidine have been reported by Scholtz and Wassermann (3) as solids melting at 122 and 126°C., respectively. Several other workers, however, have described N-*p*-tolylpiperidine as a liquid at room temperature, and this has been confirmed in the present investigation. It is possible that the constants given in the paper by Scholtz and Wassermann are for the hydrobromide salts since they prepared their compounds by the reaction of the toluidines with 1, 5-dibromopentane. N-*m*-Tolylpiperidine, as the free base, does not appear to have been reported previously.

Since there is no reason for assuming that tetrahydropyran is more reactive than tetrahydrofuran in the reaction with aromatic amines, the high yields obtained in the present study under relatively mild conditions would suggest that Yur'ev, in his investigation of the reaction of tetrahydrofuran, either failed to determine the influence of temperature or had at his disposal an alumina catalyst of lower activity than that used in this investigation. In order to confirm this point, the reaction of aniline with tetrahydrofuran has been investigated over the Alcoa alumina catalyst and an 88% yield of N-phenylpyrrolidine was obtained at 290°C. as compared to the 45.5% reported by Yur'ev at 400°C.

EXPERIMENTAL AND RESULTS

Materials

Tetrahydropyran was kindly supplied by E. I. du Pont de Nemours and Company (Inc.). The commercial product was dried over Drierite and redistilled, the fraction boiling at 87-88°C. being used in the investigation.

Tetrahydrofuran was obtained from the Celanese Chemical Corporation. It was dried over Drierite, distilled, and a mid-cut boiling over a two-degree range retained.

Aniline (Baker and Adamson Purified Grade) was redistilled, b.p. 184-184.2°C. *o*-Toluidine (Baker and Adamson Purified Grade), *m*-toluidine (Eastman), and *p*-toluidine (Baker and Adamson Purified Grade) were used without further purification.

Catalyst

The catalyst used in all experiments reported in this paper was Alcoa Activated Alumina (Grade F-1, 4-8 mesh) supplied by the Aluminum Company of America. Following each run, the catalyst was regenerated by passing air over the catalyst bed for 24 hr. at 400°C. This served to remove adsorbed reactants and products. The presence of carbonaceous material on the catalyst was noted only after runs carried out at an elevated temperature, 375-400°C.

The activity of the catalyst, as measured by the yield of N-phenylpiperidine formed under a given set of conditions, was found to depend to a considerable extent upon its previous history. A fresh catalyst exhibited relatively low activity. Following regeneration in the manner stated, however, a slightly higher yield of product was obtained and the catalyst continued to improve in activity with successive runs and regenerations reaching a maximum at about the sixth or seventh run. This high activity was maintained during the course of the next 9 to 10 runs. (A run normally consisted of a total charge of 140 ml. of mixed reactants.) It was later found that a pretreatment of fresh catalyst by passing air over the catalyst bed for 72 hr. at 400°C. was effective in bringing it to a condition of maximum activity. All experiments reported in this paper were performed using a catalyst either pretreated in the manner described, or one which had been used for no less than six and no more than 15 runs.

The improved activity of the catalyst following prolonged heat treatment may be attributed to a conversion of some inactive boehmite present in the catalyst to γ-alumina, the catalytically active form (**2**). The falling-off in activity with continued usage would suggest a slow conversion of the γ-alumina into the inactive corundum form.

Apparatus and Procedure

The catalysis apparatus consisted of two zones, preheater and catalyst, each with separate heat control. The preheater was a vertical pyrex glass tube, 30 mm. O.D. and about 18 in. long, packed for a depth of 12 in. with marble chips. Heat was supplied by a 700 watt Chromel A wire heater wound on the spiral grooves of a 12 in. alundum refractory surrounding the tube. The lower end of the preheater was connected by means of a ground joint to the upper end of the catalyst tube, 30 mm. O.D. and about 34 in. in length, extending at an angle of 120° with respect to the preheater. This tube was packed with 200 ml. of catalyst which occupied a mid-section of the tube for a length of about 15 in. Heat for the catalyst zone was supplied by two heaters, similar to that used for the preheater, placed end to end. A thin copper tube was fitted snugly inside the refractory heaters to assist in maintaining a uniform temperature throughout the length of the catalyst bed. Both the preheater and catalyst zones were

suitably insulated, and temperatures in each were measured by means of thermocouples movable along wells concentric with the tubes.

The reactants, mixed in the desired ratio, were introduced by means of a constant-feed device into the upper end of the preheater, where they were vaporized and preheated to the desired temperature before entering the catalyst tube. The reaction products passing from the catalyst zone were condensed by means of a Friedrich condenser and collected in a suitable receiver. All connections were made with ground joints. In order to establish equilibrium conditions, a prerun of 40 ml. was made during which temperatures and feed-rate were given final adjustment. A run usually consisted of 100 ml. of mixed reactants in addition to the prerun.

The liquid products consisted of two phases, aqueous and organic, of about the same density. The organic phase was salted out with sodium chloride, separated, and dried over sodium hydroxide. The product was carefully frac-

TABLE I
IDENTIFICATION OF PRODUCTS

Compound	B.p.,* °C.	n_D^{25}	Derivatives
N-Phenylpiperidine	129-132 (20 mm.)	1.5601	Picrate m.p. found: 147.5-148.5°C.† lit.: 148°C. Hydrobromide m.p. found: 235-236°C.† lit.: 235°C.
N-*p*-Tolylpiperidine	140.8-142.0 (16 mm.)	1.5502	Picrate m.p. found: 175.9-176.2°C.† lit.: 176°C.
N-*m*-Tolylpiperidine	138-139 (12 mm.)	1.5535	Picrate m.p. found: 176.3-176.6°C.† Hydrochloride calc. for $C_{12}H_{18}NCl$: Cl, 16.75% found: Cl, 16.97, 17.04%
N-*o*-Tolylpiperidine	141.2-141.9 (28 mm.)	1.5392	Picrate m.p. found: 153.8-154.1°C.† Hydrochloride calc. for $C_{12}H_{18}NCl$: Cl, 16.75% found: Cl, 16.78, 16.81%
N-Phenylpyrrolidine	135-138 (20 mm.)	1.5823 (n_D^{20}) 1.5827 (n_D^{20}) (lit.)	Picrate m.p. found: 119.5-120.0°C.† lit.: 117-118°C.

* *Uncorrected.*
† *Corrected.*

tionated, using an 18 in. column packed with 3/32 in. glass helices, first under normal pressure to remove low-boiling material and unchanged cyclic ether, and finally under reduced pressure to recover excess amine. The N-arylpiperidine remaining was then distilled in an ordinary Claisen flask under reduced pressure. Some high-boiling residue usually remained in the distillation flask.

The products from the reactions of tetrahydropyran with aniline, *m*-toluidine, and *p*-toluidine, and from tetrahydrofuran with aniline, distilled over a three-degree range and were considered to be essentially pure compounds. This was further demonstrated in each case by a fractional distillation during which the boiling point and refractive index of the distillate remained constant. The product from the reaction of tetrahydropyran and *o*-toluidine, on the other hand, distilled over a much wider range and, in addition, there was a high-

boiling fraction and considerable residue. This necessitated a careful fractionation of the product from each run in order to obtain the N-*o*-tolylpiperidine as a narrow-boiling fraction.

The products which have been previously reported in the literature, N-phenylpiperidine, N-*p*-tolylpiperidine, and N-phenylpyrrolidine, were identified by their boiling points and the melting points of their picrate derivatives. The new compounds, N-*o*-tolylpiperidine and N-*m*-tolylpiperidine, were converted to their hydrochloride salts which were then analyzed for chlorine gravimetrically; picrate derivatives were also prepared.

Physical constants of all products and other data for their identification are found in Table I.

Reaction of Tetrahydropyran with Aniline

The effect of temperature on the reaction of tetrahydropyran with aniline is shown in Table II. Below 300°C., a relatively low yield of N-phenylpiperidine

TABLE II

EFFECT OF TEMPERATURE ON THE REACTION OF TETRAHYDROPYRAN WITH ANILINE
(Ether–aniline molar ratio: 1:2)
(Feed rate: 0.321 moles of mixed reactants per hour per 100 ml. of catalyst)

Run No.	Temp., °C.	Moles recovered per mole charged		Residue, gm. per 100 gm. N-PP**	% Yield of N-PP** based on:		
		THP*	Aniline		THP* charged	THP* consumed	Aniline consumed
57	290	0.086	0.563	3.1	84.7	92.6	94.5
14	300	0.023	0.499	3.8	92.0	94.0	93.3
11	310	0.016	0.500	3.6	92.0	93.2	92.0
16	325	0.000	0.504	4.6	91.0	91.0	91.8
17	335	0.000	0.502	4.3	91.8	91.8	91.0
18	350	(0.004)†	0.521	10.9	84.1	84.1	86.2
21	375	(0.043)†	0.550	14.1	71.9	71.9	76.0
2	400	(0.078)†	0.662	††	58.5	58.5	86.6

* *Tetrahydropyran.*
** *N-Phenylpiperidine.*
† *Mixed pentadienes (b.p. 40-46°C.) expressed as moles per mole THP charged.*
†† *Not determined.*

based on ether charged was obtained. This was due to an incomplete reaction as indicated by the presence of unreacted ether and an aniline recovery in excess of 0.5 moles per mole charged. Yields based on reactants consumed, on the other hand, were well over 90%, demonstrating that under these conditions side-reactions were occurring to a minor extent. Above 350°C., the side-reactions became more extensive and resulted in the formation of a considerable amount of high-boiling material and a volatile fraction (b.p. 40-46°C.) identified as a mixture of normal pentadienes. (Some of the high-boiling material may have been formed by polymerization of these dienes.) It is evident from the data on the recovery of aniline and the yields of the product that tetrahydropyran was involved to a greater extent than aniline in these side-reactions. Nevertheless, the small reduction in the yields based on aniline consumed would indicate that this reactant also enters into side-reactions at

the more elevated temperatures. Maximum yields of N-phenylpiperidine were obtained in the temperature range 300-335°C., where a favorable balance was achieved between the extent of conversion and the formation of the dienes and other side-reaction products.

The effect of the ratio of the reactants on the yield of N-phenylpiperidine is shown in Table III. It is apparent from these results that an excess of aniline was required to achieve high yields of the desired product. This excess need not be large, however; at 325°C., an 87.1% yield (based on ether charged) was obtained using an ether–aniline ratio of 1: 1.2 compared to 91.0% when this ratio was 1: 2. The data presented in this table provides further evidence that

TABLE III

EFFECT OF RATIO OF REACTANTS ON THE REACTION OF TETRAHYDROPYRAN WITH ANILINE
(Feed rate: 0.318 ± 0.003 moles of mixed reactants per hour per 100 ml. of catalyst)

Run No.	Molar ratio, THP: aniline	Diene fraction, moles per mole THP	Residue, gm. per 100 gm. N-PP	% Yield of N-PP based on:			
				THP charged	THP consumed	Aniline charged	Aniline consumed
Temperature: 300°C.							
14	1:2	0.00	3.8	92.0	94.0		93.3
47	1:1.2	0.00	4.1	78.8	93.8		96.3
33	1:1	0.00	3.3	73.8	91.6	73.8	97.6
42	2:1	0.00	6.9		82.8	89.4	89.4
Temperature: 335°C.							
17	1:2	0.00	4.3	91.8	91.8		91.0
35	1:1	0.015	6.0	81.8	84.6	81.8	94.9
40	2:1	0.031	17.2		63.0	88.7	88.7

side-reactions mostly involve the ether reactant. At 335°C., a 1: 1 molar ratio of reactants gave a yield of N-phenylpiperidine based on ether consumed which was 10% lower than that based on aniline consumed. This difference becomes as great as 25% when the ether–aniline ratio was 2: 1.

Feed-rate was found not to be an important variable in the reaction. At 300°C. and an ether–aniline ratio of 1: 2, an increase in feed-rate from 0.321 moles of mixed reactants per hour per 100 ml. of catalyst to 1.28 moles resulted in a decrease in the yield of N-phenylpiperidine of only 5%. The yields based on ether and aniline consumed were not affected.

Reaction of Tetrahydropyran with the Toluidines

The results of this study are summarized in Table IV. Excellent yields of N-tolylpiperidines were obtained with *m*- and *p*-toluidine. With *o*-toluidine, on the other hand, yields were much lower and high-boiling material was formed in considerable quantity at temperatures as low as 325°C. This result is indeed not surprising since Scholtz and Wassermann (3) have shown

TABLE IV

REACTION OF TETRAHYDROPYRAN WITH THE TOLUIDINES

(Ether–toluidine molar ratio: 1: 2)

(Feed rate: 0.285 moles of mixed reactants per hour per 100 ml. of catalyst)

Run No.	Temp., °C.	Moles recovered per mole charged		High-boiling fraction and residue, gm. per 100 gm. N-TP*	% Yield of N-TP* based on:		
		THP	Amine		THP charged	THP consumed	Amine consumed
p-Toluidine							
53	300	0.038	0.511	4.0	90.8	94.1	91.5
52	325	0.000	0.501	3.6	92.5	92.5	92.5
m-Toluidine							
58	325	0.000	0.495	4.8	94.3	94.3	92.6
o-Toluidine							
55	300	0.290	0.758	6.8	44.9	62.1	83.8
54	325	0.086	0.653	11.3	61.3	67.0	82.8
56	340	0.019	0.618	14.6	66.3	67.5	82.7

* *N-Tolylpiperidine.*

that the reaction of 1, 5-dibromopentane with *o*-toluidine failed to give the expected N-*o*-tolylpiperidine, but instead, yielded an open-chain compound identified as 1, 5-di-*o*-toluinopentane. They attributed this result to the steric effect of the ortho methyl group; the reduced yield of N-*o*-tolylpiperidine in the present investigation may be similarly explained.

Reaction of Tetrahydrofuran with Aniline

The results of three experiments involving these reactants are given in Table V. It is apparent that even milder conditions are effective for this reaction. This would clearly indicate that the temperature of 400°C. used by Yur'ev in his investigation of the reaction was much too high and that extensive side-reactions were responsible for his low yield of 45.5%.

TABLE V

REACTION OF TETRAHYDROFURAN WITH ANILINE

(Ether–aniline molar ratio: 1: 2)

(Feed rate: 0.342 moles of mixed reactants per hour per 100 ml. of catalyst)

Run No.	Temp., °C.	Ether recovered: moles per mole charged	% Yield N-phenylpyrrolidine based on ether charged
THF 4	290	0.01	88.0
THF 3	300	0.00	79.6
THF 1	310	0.00	73.9

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INVESTIGATION OF THE FORMS OF PHOSPHORUS IN NEUTRON-BOMBARDED PHOSPHATES

NATURE OF THE PHOSPHORUS-32[1]

By J. G. A. Fiskell, W. A. DeLong, and W. F. Oliver

ABSTRACT

Evidence concerning the forms of phosphorus-32 occurring in neutron-bombarded calcium phosphates has been obtained using carrier ions for the different forms, and estimations of the proportional amounts present in these forms have been made. Ortho-, hypo-, pyro-, and metaphosphate forms of phosphorus-32 have been found as activity in the precipitation of the respective carriers; hypophosphate appeared to be an invariable and major component.

INTRODUCTION

The chemistry of the Szilard-Chalmers reaction (15) has been discussed by Libby (8, 9), Maddock (11), Süe (14), and Williams (17). The general conclusions reached were that an atom receiving a neutron recoils with such force on the subsequent emission of the gamma ray that the chemical bonds must be broken in nearly all instances, and that, when this reaction occurs in solution the retention by the nascent atom of its original chemical form is less than in those cases where the salt was bombarded as a solid.

In the case of neutron-bombarded phosphates, Libby (8) reported retentions of the order of 30 to 50%, the extent of the retention being dependent on the experimental conditions. On the basis of the assumption that all the phosphorus precipitable by magnesia reagent was in the orthophosphate form, Aten (1), Libby (8), and Thomas and Nicholas (16) concluded that 50% of the phosphorus-32 produced by neutron-bombardment of solid sodium phosphate occurred in solution as orthophosphate. The radioactivity of the filtrates from the separations using magnesia mixture was considered by these authors to be from phosphite-P^{32}.

Wilson (18) and others (6, 13) have reported that exchange reactions between labeled phosphate and phosphite do not occur. A similar conclusion respecting the possibility of exchange reactions of labeled orthophosphate with pyrophosphate or metaphosphate, and of labeled pyrophosphate with metaphosphate was reached by Hull (5). In these investigations also, it was assumed that all the phosphorus precipitable by magnesia reagent was in the orthophosphate form.

One of the present writers (3) has presented evidence that phosphite and orthophosphate may react in aqueous solution to form hypophosphate. He also found that, although magnesia mixture will precipitate all of the radioactive phosphorus from a solution containing inactive hypophosphate, inactive phosphite, and radioactive orthophosphate, some of the phosphorus-32 in such a solution escapes precipitation as ammonium phosphomolybdate. These

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Contribution from the Department of Chemistry and Tracer Laboratory, Faculty of Agriculture, McGill University, Macdonald College, Que., Canada. Macdonald College Journal Series No. 289.

observations suggested that all the phosphorus precipitable by magnesia mixture from solutions containing neutron-bombarded phosphate might not be in the orthophosphate form, and that hypophosphate might occur or be formed in such solutions. It was, therefore, decided to investigate further the nature of the chemical forms of phosphorus present in neutron-irradiated phosphates, with particular regard to calcium phosphates which are of special significance for agriculture.

EXPERIMENTAL

The scheme and methods of analysis followed in the estimation of the forms of phosphorus present before bombardment are given in Fig. 1. It may be remarked that experiment showed that hypophosphate interferes in the estimation of the pyrophosphate content of calcium phosphates by the methods employed. Analysis for hypophosphate, however, showed that the content of this form in the materials under investigation was negligible.

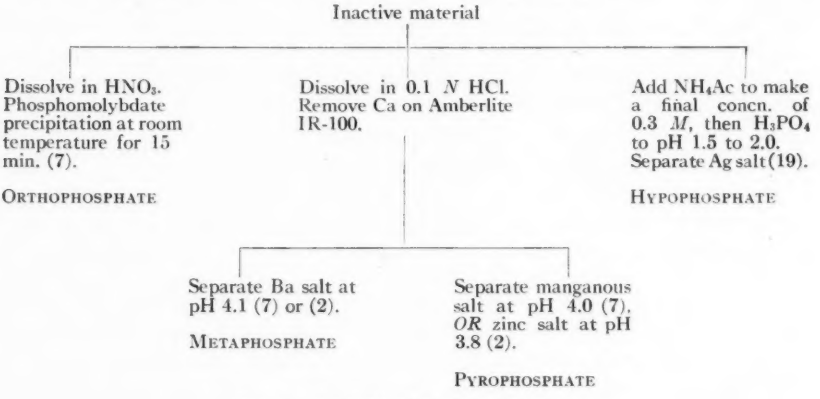
Inactive material
Dissolve in HNO_3. Phosphomolybdate precipitation at room temperature for 15 min. (7).
ORTHOPHOSPHATE
Dissolve in 0.1 *N* HCl. Remove Ca on Amberlite IR-100.
Add NH_4Ac to make a final concn. of 0.3 *M*, then H_3PO_4 to pH 1.5 to 2.0. Separate Ag salt (19).
HYPOPHOSPHATE
Separate Ba salt at pH 4.1 (7) or (2).
METAPHOSPHATE
Separate manganous salt at pH 4.0 (7), *OR* zinc salt at pH 3.8 (2).
PYROPHOSPHATE

FIG. 1. Analysis of inactive materials.

The phosphates investigated, the proportions of the forms of phosphorus present as found by analysis before neutron-bombardment, and the activity present after bombardment are listed in Table I.

The quantitative determination of phosphorus, both before and after neutron-irradiation, was performed by the colorimetric method of Gerritz (4), precautions being taken to ensure that all of the phosphorus was in the orthophosphate form. Thus, in the analysis for total phosphorus content of bombarded materials, a 0.100 gm. sample was dissolved in concentrated nitric acid and all of the phosphorus converted to orthophosphate by treatment with ammonium persulphate and perchloric acid before proceeding with the colorimetric estimation.

Estimation of the Forms of Phosphorus-32

In the estimation of the total radioactivity of neutron-bombarded materials due to phosphorus-32, two procedures were employed, namely: (*a*) A sample

of the bombarded material (0.100 gm.) was placed directly under a counter of the end-window type; the effect of the radioactivity of calcium-45 was eliminated by inserting 63 mgm. per cm.^{2} of aluminum between the surface of the sample and the chamber of the Geiger-Müller tube. (*b*) The phosphorus was converted quantitatively to orthophosphate as described above and then precipitated as ammonium phosphomolybdate (7). The precipitate was converted to magnesium ammonium phosphate hexahydrate (3, 10) and the activity of this precipitate was measured under the same geometrical conditions as in procedure (*a*). Under the experimental conditions, the linear relationship between counts per minute and weight of sample indicated negligible self-absorption. The activities obtained for similar weights of sample analyzed by the two procedures were in close agreement. It must be emphasized, however, that prolonged treatment with nitric acid and perchloric acid

TABLE I

Sample number	Substance	Forms of phosphorus	Activity as P^{32}
N.R.C. 510-2	Monocalcium* phosphate	80% orthophosphate 12% pyrophosphate	1 mc./10.0 gm.
N.R.C. 510-3	Monocalcium** phosphate	100% orthophosphate	1 mc./10.0 gm.
N.R.C. 583-2	Tricalcium*** phosphate	96% orthophosphate	0.5 mc./6.2 gm.
N.R.C. 510-4	Calcium pyrophosphate†	100% pyrophosphate	1 mc./1.69 gm.
N.R.C. 583-1	Calcium pyrophosphate (commercial)	72% pyrophosphate 18% metaphosphate 10% orthophosphate	0.5 mc./5.0 gm.

*, **, ****C.P. reagents dried at 105°C. for 12 hr.*

†Synthesized by one of the writers (J. G. A. F.) from C.P. tetrasodium pyrophosphate and C.P. calcium chloride dihydrate.

plus ammonium persulphate is required to ensure that all the phosphorus of neutron-bombarded calcium phosphates has been converted to the orthophosphate form. The efficiency of this conversion must always be established by examination of the filtrates for evidence of radioactivity from phosphorus-32.

In the estimation of the forms of phosphorus-32 in bombarded materials 0.100 gm. samples were mixed with 0.05 gm. portions of each of the following substances as carriers, namely, calcium hypophosphate, calcium pyrophosphate, sodium polyphosphate, and sodium 'hexametaphosphate'. The polyphosphate, hypophosphate, and pyrophosphate carriers were prepared by one of the writers (J. G. A. F.). In the case of salts containing little or no orthophosphate before bombardment 0.100 gm. of magnesium ammonium phosphate hexahydrate also was added as carrier.

The analytical scheme used for bombarded materials plus carriers is summarized in Fig. 2.

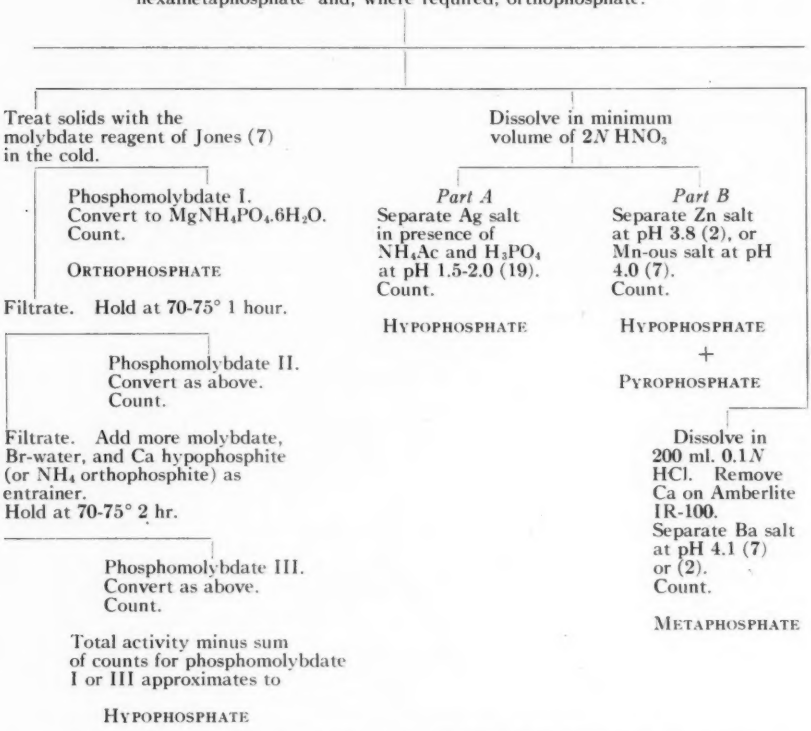
Carriers added: hypophosphate, pyrophosphate, polyphosphate, 'hexametaphosphate' and, where required, orthophosphate.
Treat solids with the molybdate reagent of Jones (7) in the cold.
Dissolve in minimum volume of 2N HNO3
Phosphomolybdate I. Convert to MgNH4PO4.6H2O. Count.
ORTHOPHOSPHATE
Part A
Separate Ag salt in presence of NH4Ac and H3PO4 at pH 1.5-2.0 (19). Count.
HYPOPHOSPHATE
Part B
Separate Zn salt at pH 3.8 (2), or Mn-ous salt at pH 4.0 (7). Count.
HYPOPHOSPHATE + PYROPHOSPHATE
Filtrate. Hold at 70-75° 1 hour.
Phosphomolybdate II. Convert as above. Count.
Filtrate. Add more molybdate, Br-water, and Ca hypophosphite (or NH4 orthophosphite) as entrainer. Hold at 70-75° 2 hr.
Phosphomolybdate III. Convert as above. Count.
Total activity minus sum of counts for phosphomolybdate I or III approximates to
HYPOPHOSPHATE
Dissolve in 200 ml. 0.1N HCl. Remove Ca on Amberlite IR-100. Separate Ba salt at pH 4.1 (7) or (2). Count.
METAPHOSPHATE

FIG. 2. Analysis of bombarded materials plus carriers for forms of phosphorus-32.

In the analysis for forms of phosphorus-32 separate 0.100 gm. samples of neutron-bombarded material were taken for estimation of each of the forms sought, namely, orthophosphate (and hypophosphate by difference), hypophosphate, hypophosphate plus pyrophosphate (for estimation of the latter by difference), and metaphosphate. With the object of reducing interactions and hydrolytic effects, the time interval between solution of the bombarded phosphate-carrier salts mixtures and the separation of the chemical forms sought was made as short as possible. For all separations, except that of barium metaphosphate, the elapsed time was of the order of 15 min. About 45 min. were required to effect the separation of metaphosphate from the mother liquor.

Radioactivity counts were made directly on the silver, zinc, manganous, and barium salts. Whenever the activities of the silver and the zinc (or manganous) salts were not in essential agreement, the difference was assumed to be due to phosphorus-32 in the pyrophosphate form. All radioactive measurements were made at constant geometry. Corrections for decay and self-absorption

TABLE II

Material bombarded	Forms of phosphorus-32 estimated					
	Total	Ortho-phosphate	Hypo-phosphate	Hypo- + pyro- phosphate	Pyro-phosphate by difference	Meta-phosphate
	Counts per minute					
N.R.C. 510-2 Monocalcium phosphate	2830	849	1390	1740	350	Not
	2860	868	1251	1810	539	detd.
	2846	841	1175	1620	445	
Estimated % of P^{32}	100	30	45	61	16	
N.R.C. 510-3 Monocalcium phosphate	2717	1195	918	Not	Not	Not
	2730	1184	950	detd.	detd.	detd.
	2725	1165	907			
Estimated % of P^{32}	100	43	34			
N.R.C. 583-2 Tricalcium phosphate	15852	6119	5608	Not	Not	5086
	16005	6518	6097	detd.	detd.	5213
	15887	5625	5860			4940
Estimated % of P^{32}	100	38	36	—	—	32
N.R.C. 510-4 Calcium pyrophosphate	23007	183	4807	18094	13227	3453
	23642	192	3220	18803	15583	4065
	23338	128	6108	18400	12292	3100
Estimated % of P^{32}	100	0.7	20	79	59	15
N.R.C. 583-1 Calcium pyrophosphate	14244	2155	4566	11536	6970	Not
	14300	2100	3955	11400	7445	detd.
	14419	2139	4323	11413	7090	
Estimated % of P^{32}	100	14	30	80	50	—

were applied, and correction for the aluminum absorber was made in case of samples which were screened for calcium-45 interference.

It may be noted that experiment indicated that the polyphosphate added as carrier was not precipitated under the conditions used for the separation of phosphomolybdate I or of the silver, zinc, manganous, or barium salts.

The experimental data obtained in the carrier precipitation analysis are summarized in Table II. It may be noted that in calculating the recovery of radioactivity either the counts in the column headed hypophosphate plus

pyrophosphate or those in the individual columns for these forms may be used, but not both.

The presence of phosphorus-32 in the hypophosphate form is indicated in all the salts investigated and from the data presented in Table II it seems to constitute a major form. According to evidence reported previously (3), it is possible that the hypophosphate was formed on dissolving the bombarded materials by interaction of phosphite with phosphate. An alternative possibility is that hypophosphate formation took place within the crystal at the time that the recoil atom was situated favorably for recombination with the shattered fragments of the molecule.

Additional evidence for the presence of phosphorus-32 in the form of hypophosphate was obtained by use of ammonium molybdate precipitation (Fig. 2). Examination of the results obtained by this technique revealed amounts of unprecipitable phosphorus-32 which coincided reasonably well with those estimated as hypophosphate by carrier precipitation. One of the writers (3) reported previously that hypophosphate in solutions containing calcium was very difficult to convert to the orthophosphate form under the conditions just

TABLE III

COMPARISON OF ESTIMATES OF HYPOPHOSPHATE–PHOSPHORUS-32

Materials	Unprecipitable phosphorus-32	Phosphorus-32 precipitated with hypophosphate carrier
	Counts per minute	
N.R.C. 510-2 Monocalcium phosphate	1388	1390
	1214	1251
	1294	1175
Estimated % of P^{32}	46	45
N.R.C. 510-3 Monocalcium phosphate	698	918
	876	950
	803	907
Estimated % of P^{32}	29	34
N.R.C. 583-2 Tricalcium phosphate	5123	5608
	4636	6097
	5556	5860
Estimated % of P^{32}	33	30
N.R.C. 583-1 Calcium pyrophosphate	5053	4566
	5752	3955
	5002	4323
Estimated % of P^{32}	37	30

described, also, that very little or none of the hypophosphate in such solutions was precipitable by ammonium molybdate.

The experimental data are presented in Table III.

All of the bombarded samples were tested for the presence of phosphorus-32 in the form of phosphine. This was done by aspiration of the gases present in the containers, as received from the Chalk River Laboratories, through dry absorbent cotton (for removal of dust particles) into cotton moistened with an ammoniacal solution of silver nitrate, the latter then being tested for radioactivity. In no instance was a positive result obtained. However, a sample of calcium hypophosphite prepared by one of the writers (J. G. A. F.) did give a positive reaction for the presence of radioactive phosphine when examined in this manner after neutron bombardment.

Further examination of this bombarded calcium hypophosphite, using the methods described above, indicated that 25% of the phosphorus-32 was present as orthophosphate and 7% as hypophosphate. Less than 3% of the radioactivity was found in the pyrophosphate and metaphosphate carrier precipitates separated from the solution containing the neutron-bombarded calcium hypophosphite. In this material the phosphorus-32 not precipitable by ammonium molybdate amounted to about 46% of the total. The discrepancy between this result and that obtained by carrier precipitation of hypophosphate may have been a consequence of phosphite–phosphate reaction over the longer period of time, or, since radioactive phosphine was found, some phosphorus-32 may have been present as phosphide. Mellor (12) has recorded several reactions of lower oxidation forms of phosphorus which lead to the production of phosphine.

The major conclusions drawn from these experiments are (*a*), that when calcium phosphates are subjected to neutron bombardment in the solid state there is considerable retention of the original chemical form, (*b*), that a major fraction of the remainder of the phosphorus-32 produced appears in solution as hypophosphate, and (*c*) that when such materials are used for labeling of inactive phosphates, the greatest care must be taken to ensure that the phosphorus-31 and phosphorus-32 are present in the same chemical form.

ACKNOWLEDGMENT

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THE OXIDATION OF FERROUS SULPHATE SOLUTIONS BY γ-RAYS—THE ABSOLUTE YIELD

By T. J. Hardwick

ABSTRACT

The absolute value of the yield of ferric ion on the irradiation of ferrous sulphate in 0.80 *N* sulphuric acid by γ-rays has been determined using the Bragg–Gray cavity principle. Sources of error in the measurements were reduced as much as possible. The yield obtained, 20.8 ± 0.3 ferric ions per 100 ev. absorbed, agrees well with Miller's value of 20.7 molecules per 100 ev.

In a recent paper Miller (2) has proposed the use of ferrous sulphate in 0.8 *N* sulphuric acid as a chemical dosimeter for the measurement of absorbed ionizing radiation. Using the Bragg–Gray cavity principle, he has investigated several methods of comparing ionization in an air-filled cavity with chemical change in a ferrous sulphate solution in a similar cavity under identical conditions of irradiation. A cavity in the form of a thin annulus surrounding a γ-ray source proved most satisfactory. A comparison of the ion current measured in air and the rate of oxidation of ferrous ion gives an absolute value of the yield.

Using this technique, Miller obtained a value of 19.7 micromoles per liter per kiloroentgen as the yield of the reaction. This may be expressed as 20.3 ferric ions produced per 100 ev. of energy absorbed, a unit which is becoming more popular among radiation chemists. In view of the importance of this value as a reference figure, a survey of Miller's experiments seems in order.

Six chemical experiments were made to determine the yield. These show among themselves a deviation from the mean of ± 5%. There is no indication of the error involved in making an ion chamber measurement, in the measurement of the high resistor, or in the reading of the back-off voltage. From the experience of the present writer, these will be taken as ± 3% under the conditions used by Miller. It seemed worthwhile to repeat this experiment taking steps to reduce the error as much as possible, and indicating the magnitude of errors in the work.

Miller (2) and previous workers have shown that in the concentration range 10^{-3} to 10^{-4} *M* ferrous ion, the yield of ferric ion is independent of the ferrous ion concentration. This was reconfirmed before starting on the present work.

The theoretical argument for the validity of this work will not be repeated here. Excellent reviews of the cavity principle have been made by Miller (2) and by Wang (3). However, as the main difference between this work and Miller's is in the refinement of measurement, a description of the apparatus and procedures will be given in greater detail.

EXPERIMENTAL

Five identical polystyrene cells were made to the specifications of Fig. 1. The volumes of each were measured gravimetrically. Two cells whose annulus

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volumes agreed within 0.03% were used for the irradiation of solutions. The remaining three were converted into ion chambers by coating the vertical surfaces of the annuli with a thin film of colloidal graphite.

The irradiation apparatus was that used by Miller. The cells could be interchanged in the center of a large block of lead by withdrawing a removable section of the block. A 2 curie cobalt source could be lowered through the top

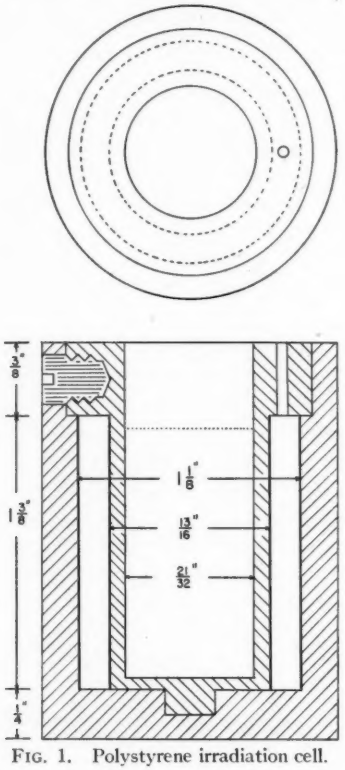

FIG. 1. Polystyrene irradiation cell.

of the block to fit snugly in the center of the cell. The rate of chemical change in solution could be compared with the ion current in the ion chambers.

Ionization Measurements

Electrical connections were made from the graphite walls of the ion chambers through the top of the cell by means of thin copper wires. A potential of 300 v., which was found to be sufficient to saturate the ion chamber, was put across the chamber. The ion current collected on the collector electrode was allowed to leak to ground through a high resistor, which had a value of $(5.005 \pm 0.005) \times 10^7$ ohms d-c. The potential across this resistor was measured by a Leeds and Northrup type K2 potentiometer, using a Lindemann

type electroscope as a null instrument. The sensitivity of the electroscope was set at 300 divisions per volt, and null measurements were possible to about one-fifth of a division; hence the sensitivity of the potential measurement was about 0.6 mv. As the potential across the resistor was about 300 mv., the sensitivity of the readings was $\pm$ 0.2%.

A reversing switch permitted the polarities of the electrodes to be interchanged in order to determine the effect, if any, of stray ion currents, arising usually from leaking insulation. No noticeable change in the ion current was found.

The contribution to the ion current from ion collection outside the annulus was determined by replacing the ion chamber with a dummy polystyrene cell of identical construction, in which the electrical connections terminated in the polystyrene. The ion current in this case was less than 0.2% of that in the normal ion chamber.

Ion chamber measurements were made at least daily over two separate periods of six weeks each. The ion current was reduced to conditions of N.T.P. As the irradiation unit was kept in an air conditioned, thermostatted room (21°C.), temperature variation was slight. A correction was also made for the decay of the cobalt 60 source, using a half-life of 5.26 years.

Three ion chamber cells were used to prevent any error arising from leaking insulation, poor connections, etc. It was found that when these cells were interchanged and a small correction made in the ion current for the volume differences (less than 0.3%), readings from all cells agreed within experimental error; hence it was concluded that the ion chambers were properly constructed and gave a true measure of the energy absorbed.

Measurement of Chemical Change

1. *Preparation of Solutions*

Solutions were made using Baker and Adams Reagent Grade ferrous ammonium sulphate, Nichols C.P. sulphuric acid, and water which had been distilled successively from alkaline permanganate and from an alkaline suspension of manganous hydroxide. The water was made acid with the appropriate amount of standardized concentrated sulphuric acid. The ferrous ammonium sulphate was weighed and dissolved in the acid solution. The ferrous ion concentration was usually about 10^{-3} *M*, while the acid concentration was maintained at 0.80 *N*. The solution was allowed to stand and was consequently air saturated.

2. *Irradiation of Solution*

The cell was washed out with the ferrous solution and then about 15 ml. more poured in. The center portion was then put in, the overflow coming through the vent hole in the top. In the final stage the cell contained solution and no air bubbles. The locking screw was then inserted to prevent the center portion from floating. The cell was irradiated for such a time that about half the ferrous ion was oxidized (about two hours). There was sufficient oxygen

present in the solution for the oxidation of this amount of iron (see Miller). No spontaneous oxidation of ferrous ion occurred on standing in the polystyrene. The addition of ammonium sulphate up to 10^{-2} M had no measurable effect on the yield; thus the ammonium sulphate introduced in the ferrous ammonium sulphate does not change with the yield.

Analysis of the irradiated solution was made in two ways. The first consisted in measuring the disappearance of ferrous ion by measuring its concentration by the *o*-phenanthroline method before and after irradiation. To a sample of the iron solution (0.5 ml. for the initial solution, 1.0 ml. for the irradiated solution) was added 0.5 ml. of a saturated aqueous solution of *o*-phenanthroline and 2 ml. of 2 M sodium acetate. The whole was diluted to 10 ml. The percentage transmission was measured on a Beckman quartz photoelectric spectrophotometer at a wave length of 510 mμ and slit width of 0.04 mm. In determining the molar extinction coefficient of the ferrous-*o*-phenanthroline complex, Reagent iron wire (99.7%) was used as the primary standard. The value obtained was $\epsilon_{510} = 11517 \pm 25$. The over-all error in measurement was $\pm$ 1.5%.

In the second set of experiments, made six months later, the amount of oxidation was determined by measuring the appearance of ferric ion at a wave length of 304 mμ and a slit width of 1.2 mm. using a tungsten lamp. The molar extinction coefficient of ferric ion is 2166 ± 6 at $\lambda = 304$ mμ. As the absorption of light by ferrous ion in 0.8 N sulphuric acid solution is small ($\epsilon_{Fe^{++}304} < 1$), and the original solution was used as a blank in the spectrophotometer, the error in measurement was lower than with the *o*-phenanthroline method. Furthermore, no dilution was necessary for analysis as was required with this method. The over-all error was $\pm$ 0.8%.

RESULTS

The results of the experiments are summarized in Table I. The rate of energy absorption in air was calculated using a mean value of 31.9 ev. per ion pair for electrons produced by Co^{60} γ-rays (3). The relative electron stopping powers of air and 0.80 N sulphuric acid were considered equal for γ-rays of Co^{60}.

The yield is higher than that reported by Miller (20.3 molecules per 100 ev.). However, he used a value of 32.5 electron volts for the formation of an ion pair in air. A correction of his value gives a yield of 20.7 molecules per 100 ev.; hence the two sets of results are in very good agreement.

There is no effect of the polystyrene on reaction as is shown by the following experiment.

The rate of oxidation of ferrous ion was measured in a glass test tube in a radiation field. This test tube was then coated on the inside with a thin film of polystyrene and the irradiation repeated. The rates of oxidation agreed within 1%.

The deviation from the mean value for the rate of ferrous ion oxidation is

TABLE I

	A	B
Period of experiments	15/12/49 to 1/2/50	1/7/50 to 10/8/50
Data normalized to	1/1/50	1/7/50
Temperature, °C.	21	21
Ion current (at N.T.P.), amp.	6.276×10^{-9}	5.877×10^{-9}
Number of ion current determinations	30	18
Deviation, %	0.3	0.25
Limit of absolute error, %	0.3	0.3
Total error (ion current measurements), %	0.3	0.3
Rate of energy absorption in air, ev./cc./sec.	$1.16_4 \times 10^{11}$	$1.090_4 \times 10^{11}$
Rate of energy absorption in solution ev./ml./sec.	$1.002_6 \times 10^{14}$	0.9388×10^{14}
Rate of chemical change, moles/l./hr.	1.242×10^{-4}	1.177×10^{-4}
Number of chemical measurements	36	43
Deviation, %	1.2	1.0
Absolute error, %	1.5	0.8
Total error (chemical measurements), %	1.4	0.9
Yield, ferric ions/100 ev.	20.7	21.0
Total error, %	1.7	1.2

Mean yield = 20.8 ± 0.3 ferric ions/100 ev. absorbed

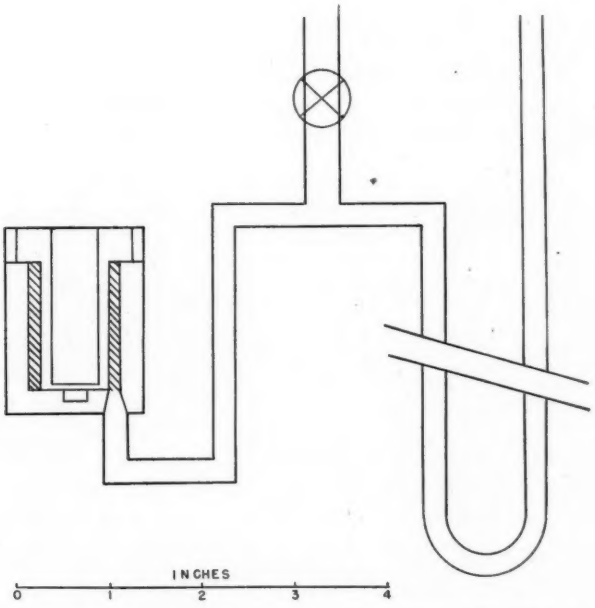

FIG. 2. Irradiation cell and apparatus to determine the effect of pressure on the ion current.

larger than expected from the reproducibility of the ferric ion analysis. No explanation is readily found.

It is essential that the ion chambers used in this experiment exhibit the properties of a true cavity, that is, the number of secondary electrons that begin or terminate in the cavity must be negligible in comparison with the number of ion pairs formed. This will be true if the ion current is proportional to the pressure of air inside the cavity (1, 3). One of the cells was converted into a pressure ion chamber by attaching through the bottom a manometer

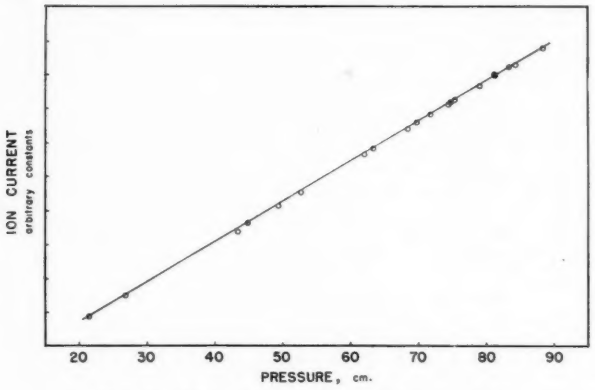

FIG. 3. Effect of pressure on the ion current.

and valve as shown in Fig. 2. The pressure was varied from 250 to 900 mm. The resulting ion currents were plotted against the pressure and a straight line obtained (Fig. 3). The annulus thus has the properties of a true cavity.

CONCLUSIONS

The yield of ferric ion in the oxidation of ferrous ion in 0.80 N sulphuric acid by γ-rays is 20.8 ± 0.3 molecules per 100 ev. This result agrees excellently with Miller's.

ACKNOWLEDGMENTS

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THE REDUCTION OF CERIC SULPHATE SOLUTIONS BY IONIZING RADIATION[1]

By T. J. Hardwick

ABSTRACT

The yield of cerous ions formed in the reduction of ceric ion in sulphuric acid solutions by X and γ-radiation is independent of cerous and ceric ion concentration, the energy of the radiation, the rate of energy absorption over a wide range, the acid concentration, and the presence of oxygen. A small negative temperature coefficient has been observed. The over-all stoichiometric equation is

$$4Ce^{4+} + 2H_2O \rightarrow 4Ce^{3} + 4H^{+} + O_2.$$

Hydroxyl radicals postulated to be produced by the radiation form water and oxygen gas. The lower limit of concentration independence is below 2×10^{-6} moles per liter.

INTRODUCTION

Chemical effects arising from the absorption of ionizing radiation by water are commonly discussed in terms of the reactions of hydrogen atoms and hydroxyl radicals, which were postulated by Weiss (22) as the primary products. Quantitative studies of the effect of ionizing radiation on water and aqueous solutions have followed five main paths:

(1) Inorganic oxidations: e.g. oxidation of ferrous ion (7, 18, 15); oxidation of nitrite ion (8); oxidation of arsenite ion and selenite ion (9).

(2) Inorganic reductions: e.g. reduction of potassium dichromate (10), reduction of persulphate ion (14), and reduction of ceric ion (3).

(3) Polymerization reactions (4, 5).

(4) Decomposition of organic solutes, including biological materials: e.g. alcohols and acids (11), deactivation of enzymes (6), and oxidation of benzene to phenol (23).

(5) Decomposition of pure water: e.g. (12, 2, 1, 19).

The reactions in the first two groups belong to the electron transfer type, where the free radicals become either hydrogen ions or hydroxyl ions.

Considerable work has been done on electron transfer oxidations, that is, reactions of hydroxyl radicals with inorganic reducing agents, particularly in the case of ferrous ions (18, 15, 16), but comparatively little is known about electron transfer reductions, i.e. reaction of hydrogen atoms with an oxidizing agent. In this field the reduction of ceric ion to cerous ion seemed an attractive subject for study, as the chemical change taking place in the ceric ion is itself a simple electron transfer reaction.

The reduction of ceric ion in sulphuric acid solutions by 50 kv. X rays was studied by Clarke (3). He found the yield to be reasonably independent of ceric ion concentration and independent of acid concentration within certain limits. The yield found was two cerous ions produced per ion pair formed. No mechanism was postulated, but a reference to Fricke's "Activated water"

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hypothesis was made. A more detailed examination of the ceric sulphate system with a view to elucidating free radical behavior appeared desirable.

Ceric sulphate solutions must be kept acidic to prevent hydrolysis or polymerization. Solutions were maintained 0.80 *N* in sulphuric acid unless otherwise stated, this concentration being chosen because most of the radiation-induced oxidation of ferrous ion has been carried out with this acid at this concentration.

EXPERIMENTAL AND RESULTS

Ceric sulphate solutions were prepared by dissolving an appropriate amount of G. F. Smith Co. ceric ammonium sulphate in 0.80 *N* sulphuric acid. The

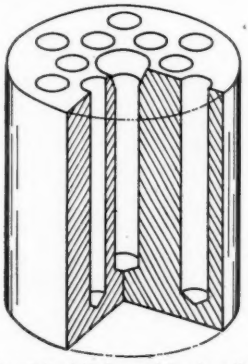

FIG. 1. Graphite block used for irradiations.

water used for preparing the solutions was successively distilled from alkaline potassium permanganate and alkaline manganous hydroxide suspension. Ceric ion solutions were allowed to stand overnight before use. At these acid concentrations, ammonium ion was found to have no effect on the reaction (cf. Miller (18)).

Analysis:— Ceric sulphate was analyzed by measuring the light absorption at a wave length of 3300 Å. by means of a Beckman Quartz Photoelectric Spectrophotometer. The value of the molar extinction coefficient in 0.80 *N* sulphuric acid was 5800. Titration with ferrous sulphate provided the initial standardization. The error in this procedure, unless otherwise specified, was about 1%.

The irradiation of solutions was carried out in a graphite block shown in Fig. 1. Two sets of concentric holes surrounded a central cavity into which a retractable source could be lowered. During irradiation the block was placed within a lead castle (not shown). Because of the fixed, reproducible geometry of the irradiation apparatus, a constant rate of energy absorption was obtained, hence the relative values of the results were quite accurate. The source used was about 2 curies of Co^{60}, corrections being made for its decay when necessary. Five-milliliter aliquots of solution were irradiated in 16 mm. O.D. pyrex tubes which fitted snugly into the concentric holes.

Dosimetry:— The rate of energy absorption was determined by measuring the rate of oxidation of a dilute air-saturated ferrous sulphate solution in 0.80 *N* sulphuric acid. The yield for the ferrous sulphate oxidation reaction, determined in a separate experiment, was taken as 20.8 ferric ions produced per 100 ev. absorbed by the solution.

A review of previous work on the effects of ionizing radiation on aqueous solutions indicated that the following variables would require investigation: ceric ion concentration, rate of energy absorption, energy of incident X or γ-rays, sulphuric acid concentration, presence of dissolved oxygen, and temperature. Of importance also is the relative ratio of cerous ion produced to oxygen gas produced, and the average energy required to reduce one ceric ion.

A. *Concentration*

Aliquots of a solution of ceric ion, 10^{-4} moles per liter, were irradiated in the graphite block for various lengths of time. The resulting amount of ceric ion reduced, expressed as cerous ion formed, is plotted in Fig. 2 as a function of

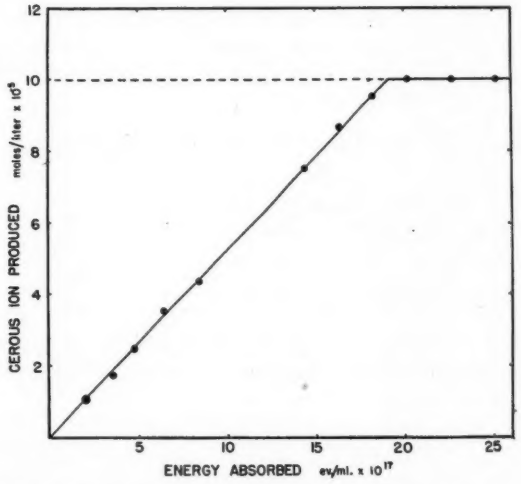

FIG. 2. Production of cerous ion as a function of energy absorbed from γ-rays. Air saturated solution.

energy absorbed. These results show that the reaction is zero-order to 100% reduction and that cerous ion is not oxidized to ceric ion by irradiation. The yield is obtained from the slope of the straight line.

Solutions of various concentrations were irradiated in the above manner. In all cases the amount of chemical change was proportional to the total energy absorbed. The yield of the reaction is tabulated for various initial concentrations of ceric ion in Table I. As will be shown later, the effect of different rates of energy absorption is negligible.

These results indicate that the yield of cerous ion is independent of the ceric

TABLE I

EFFECT OF INITIAL CERIC ION CONCENTRATION ON THE YIELD OF CEROUS ION
AIR SATURATED SOLUTIONS

Initial ceric ion concentration, moles/liter	Rate of energy absorption, ev./ml./sec. $\times 10^{13}$	Yield, cerous ions/100 ev.
11.05×10^{-3}	3.1	3.30
5.40	3.1	3.31
2.68	3.1	3.30
1.50	3.1	3.31
7.22×10^{-4}	3.1	3.33
2.32	2.6	3.29
1.00	3.2	3.30
8.7×10^{-5}	3.1	3.33
1.64	2.6	3.3 ± 0.1
1.1	2.6	3.2 ± 0.2
7×10^{-6}	2.6	3.2 ± 0.4
4.5	2.6	3.1 ± 0.6
	Mean	$3.30 \pm .03$

ion concentration over a wide range (10^{-2} M to $\backsim 2 \times 10^{-6}$ M). Even at low initial ceric ion concentrations the reaction is zero-order as well as can be established at these low concentrations. The increasing uncertainty of analysis is responsible for the wider limits of error.

B. *Rate of Energy Absorption and Energy of Incident Radiation*

The cobalt source in the graphite block was replaced successively by two radium sources. The yield of cerous ion was measured using the oxidation of ferrous sulphate as a dosimeter. According to Miller (18) the rate of energy absorption and the energy of the γ-rays have no effect on the yield of ferric ion under the conditions of these experiments. As both inner and outer holes of the graphite block were used, two rates of energy absorption were possible with each source. The ratio between the inner and outer hole results was not exactly the same for different sources, owing to the varying physical dimensions of each of the sources.

TABLE II

EFFECT OF RATE OF ENERGY ABSORPTION AND γ-RAY ENERGY ON YIELD
INITIAL CERIC ION CONCENTRATION 1.20×10^{-4} MOLES PER LITER
AIR SATURATED SOLUTION

Source	Position of solution	Rate of energy absorption, ev./ml./sec. $\times 10^{13}$	Yield, cerous ions/100 ev.
About 2 curies Co^{60}	Inner holes	3.04	3.20
	Outer holes	1.15	3.25
2 gm. Ra	Inner holes	2.38	3.15
	Outer holes	0.97	3.20
1 gm. Ra	Inner holes	1.40	3.20
	Outer holes	0.59	3.25
	Estimated experimental error $\pm$ 0.05		

A solution of ceric ion, 1.20×10^{-4} moles per liter, was used for all experiments. The results are recorded in Table II. Each yield represents the mean of six comparative runs. Further evidence for the independence of the rate of energy absorption may be found in Table I, where the natural decay of Co^{60} gives a variable rate of energy absorption.

Within experimental error there is no effect of the rate of energy absorption within a fivefold range. A limited change in the incident γ-ray energy also appears to be without effect. The energies of the respective γ-rays are of the same order however, 0.8 Mev. for radium and 1.2 Mev. for cobalt 60.

A less accurate but wider survey of the effect of the rate of energy absorption on the yield was made using a 2000 KVP 1.5 ma. X-ray machine. Two identical polystyrene cells of 10 ml. volume were constructed (Fig. 3B). One was made into an ion chamber by coating the inner wall and the central post with graphite. Appropriate electrical connections were made for the measurement of the ion current. The second cell contained the ceric sulphate solution.

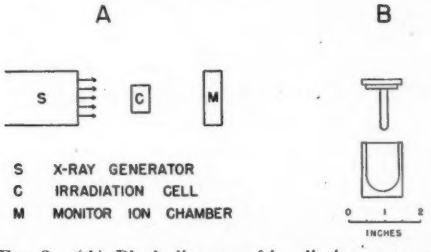

FIG. 3. (A) Block diagram of irradiation system.
(B) Irradiation cell.

The two cells could be interchanged in an apparatus of the dumb-waiter type, whereby the cell could be rapidly lowered through lead shielding into the X-ray beam while the machine was in steady operation. A recording monitor ion chamber placed behind the cell permitted a comparison of the ion current in the air cell and the chemical change in solution (Fig. 3A). The ion current in the monitor cell was calibrated against that in the irradiation cell. The energy absorbed in the aqueous solution was then estimated by integrating under the ion current curve recorded during a solution irradiation.

Owing to the wide range of rates of energy absorption used it was necessary to use different initial ceric ion concentrations. However in all cases the kinetics were of zero order. As the method of analysis used detected small traces of ceric ion, it was possible to follow the reaction to 99.95% completion when a 10^{-2} M ceric ion solution was irradiated. A strict adherence to zero-order kinetics was observed, with no apparent oxidation of cerous ion.

The rate of energy absorption was changed by varying the distance between the sample and the X-ray tube, and to a lesser extent by operating the X-ray machine at a different current. The lowest value (2.3×10^{13} ev. per ml. per sec.) was obtained by using a Co^{60} source instead of the X-ray machine.

TABLE III

EFFECT OF INTENSITY ON YIELD OF CEROUS ION

Approximate rate of energy absorption, ev./sec./ml.	Initial ceric ion concentration, moles/liter	X-ray machine operation 2000 KVP	Yield relative to Co^{60} yield
3.5×10^{16}	9.3×10^{-3}	1.5 ma.	1.05
3.2×10^{16}	1.07×10^{-3}	1.5 ma.	1.10
3.5×10^{15}	4.72×10^{-4}	1.0 ma.	1.00
2.9×10^{15}	4.8×10^{-5}	1.0 ma.	0.95
2.3×10^{13}	5.0×10^{-5}	Co^{60} γ	
	Estimated experimental error ± 0.1		

As the cells were cylindrical in shape with an inner diameter of 2.2 cm., about 1.9 cm. greater than the range of secondary electrons in water, the saturation ion current measured only a constant fraction of the energy absorbed by the solution. The ion current/chemical change ratios using the X-ray machine were therefore compared with this ratio at 2.3×10^{13} ev. per ml. per sec. (Co^{60} source). The results are recorded in Table III.

The yield of cerous ions produced by the radiation is constant even at these high rates of energy absorption. Cerous ion is not oxidized at all under these conditions.

C. *Acid Concentration*

Solutions containing about 10^{-4} moles per liter ceric ion were made up with varying amounts of sulphuric acid. Because of the ease of hydrolysis of ceric ion this variation was confined to the range 0.8 *N* to 2 *N* sulphuric acid. New extinction coefficients were determined for these solutions. The acid content was determined by the addition of a trace of hydrogen peroxide to reduce the ceric ion and subsequent titration of the solution with standard alkali.

Aliquots of these ceric ion solutions were irradiated in the graphite block, and a small correction (less than 2%) was made for the changes in electron density of the sulphuric acid solutions. The results obtained indicate that there is no effect of acid on the yield in this region. The results are recorded in Table IV.

TABLE IV

EFFECT OF ACID ON THE YIELD
INITIAL CONCENTRATION OF CERIC ION 1.00×10^{-4} MOLES PER LITER
RATE OF ENERGY ABSORPTION 2.8×10^{13} EV. PER ML. PER SEC.

Acid concentration	Yield
0.80 *N*	3.30
1.18	3.30
1.60	3.40
1.97	3.35
Estimated experimental error ± 0.05	

D. *Effect of Oxygen Gas*

Many investigators have reported an effect of oxygen in radiation induced reactions in aqueous systems, e.g. (18, 15, 4, 11). The study of the reduction of ceric sulphate by β-rays in the strict absence of oxygen cannot be carried out, as oxygen gas is one of the products. However, it is possible to reduce materially the amount of oxygen from the normal concentration of 4.5×10^{-4} M (in equilibrium with air) to a negligible amount. The presence of a gas space

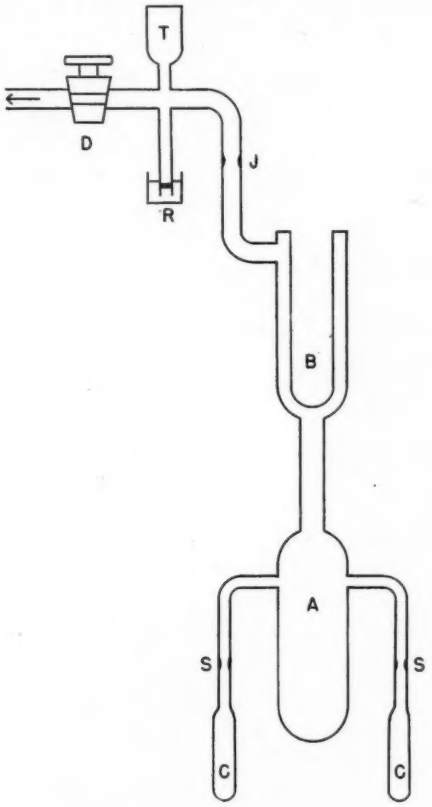

FIG. 4. Deaeration apparatus.

above the solution will tend to prevent the establishment of a large concentration of oxygen in solution.

The apparatus for the deaeration, developed in its initial form by Dewhurst (16), of solutions is shown in Fig. 4. The bulb system was cut off at J and thoroughly cleaned. Approximately 60 ml. of ceric sulphate solution was put into bulb A and the apparatus reassembled by sealing at J. Stopcock D was opened and the solution in A partly distilled onto the trap B which was

filled with liquid nitrogen. The solution usually froze as a result of this treatment and pumping was continued until the pressure was less than 1 μ as recorded by a thermocouple gauge T. Stopcock D was closed and the solution and trap allowed to come to room temperature. This evacuation plus thawing

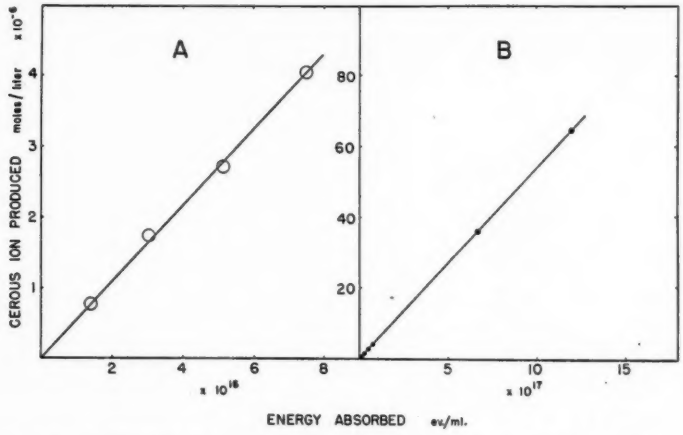

FIG. 5. Production of cerous ions as a function of γ-ray energy absorbed.
(A) Initial portion of curve.
(B) Magnified.

technique was repeated twice. After the final thawing the bulb system was sealed off at J. This procedure is estimated to lower the oxygen concentration in the solution below 10^{-9} moles per liter.

The solution in A was thoroughly mixed with any in the six sidearms C (two only shown in Fig. 5) and poured into the sidearms C up to a 5 ml. mark.

TABLE V

EFFECT OF CONCENTRATION ON THE YIELD OF CEROUS ION OXYGEN-FREE SOLUTION

Initial ceric ion concentration, moles/liter	Rate of energy absorption, ev./ml./sec. $\times 10^{13}$	Yield, cerous ion/100 ev.
175×10^{-6}	2.8	3.33
87×10^{-6}	2.8	3.33
16×10^{-6}	2.8	3.31
7×10^{-6}	2.8	3.3
1.7×10^{-6}	2.8	3.3

Each sidearm was then sealed off at S. The tubes C were irradiated in the graphite block and the remaining solution in A was analyzed to give a value for the initial ceric ion concentration.

The results with a number of ceric ion concentrations are recorded in Table V. Zero order curves were obtained in all cases. The yield in "oxygen free" systems is identical to that in air saturated systems (cf. Table I).

It was important in γ-ray reduction of air-free ceric ion solutions to establish whether small traces of oxygen play an important part in the reaction. A solution of ceric ion 7.6×10^{-5} moles per liter was deaerated and distributed to the six irradiation tubes, which were sealed off. Four irradiations were made of such a duration that less than 5% of the ceric ion was reduced. By using these solutions as a blank in the spectrophotometer and the initial

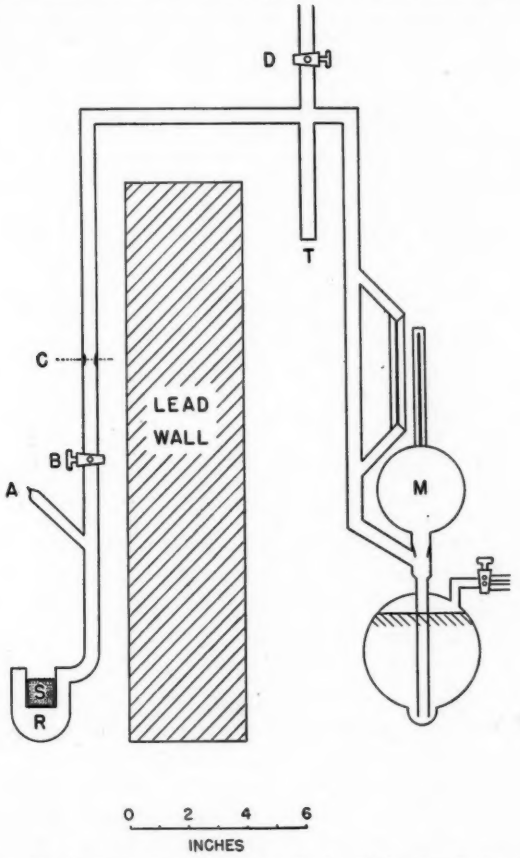

FIG. 6. Apparatus for the measurement of gas evolution during irradiation of ceric sulphate solutions.

solution as the "unknown", a very accurate measurement of the amount of chemical change was made. The results appear in Fig. 5A. The other two tubes were irradiated for a longer period. The yield was 3.27 cerous ions per 100 ev. absorbed (Fig. 5B).

The line in Fig. 5A is quite straight and passes through the origin. There is therefore no measurable induction period.

E. *Gas Production*

When a dilute aqueous solution of an oxidizing agent is irradiated with X or γ-rays, oxygen is usually a product. The rate of gas evolution was measured in the apparatus shown in Fig. 6. The irradiation vessel was separated from the McLeod gauge at C. Fifteen milliliters of a ceric sulphate solution 8.7×10^{-5} moles per liter in 0.80 *N* sulphuric acid was placed in the irradiation vessel R. This was sealed onto the vacuum apparatus described previously (Fig. 4) at the point A, stopcock B being closed and the evacuation procedure carried out. When deaeration was complete the cell was sealed off at A.

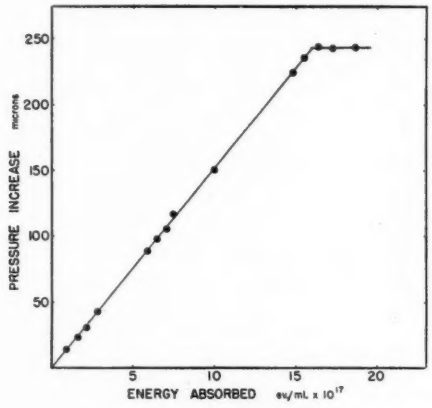

FIG. 7. Pressure increase of above solution during irradiation of ceric sulphate solutions.

The cell was sealed onto the McLeod gauge system at C. Evacuation of the McLeod gauge *M* was made through stopcock D. A 1 curie cobalt 60 source S was put in the well of the irradiation vessel.

Measurement of gas produced was carried out as follows: stopcock B was opened for 30 sec. to equalize the pressure, then shut. The water vapor in the McLeod system was frozen out in trap T by liquid nitrogen. The pressure was then measured in the normal manner. Trap T and the rest of the McLeod system were then kept above room temperature by means of an infrared lamp until the next equalization of pressure took place.

The rate of energy absorption was measured by using 15 ml. of air-saturated ferrous sulphate solution in 0.8 *N* sulphuric acid as a dosimeter. The results plotted in Fig. 7 show that gas production follows a zero order curve. From a knowledge of the rate of energy absorption and the volume of the McLeod gauge system, the yield of gas produced was calculated. Subsequent experiments where the gas was absorbed by white phosphorus showed the gas to be pure oxygen. The molar ratio of ceric ion reduced to oxygen gas evolved was 4.0 ± 0.1.

F. *Temperature*

In general, radiation-induced reactions in solution show little variation with temperature, unless secondary reactions occur which are temperature dependent. The effect of temperature on the yield of cerous sulphate produced

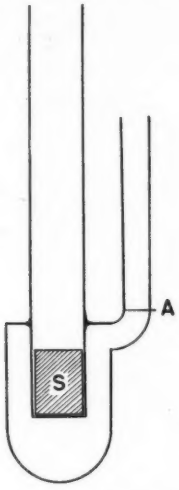

FIG. 8. Irradiation cell for the measurement of temperature effect on the γ-ray reduction of ceric sulphate solutions.

by γ-rays on ceric sulphate solution was studied in the cell shown in Fig. 8. Ceric sulphate solution was put into the cell up to the mark A (ca. 20 ml.). The unit except for the tubes was submerged in a constant temperature bath. When thermal equilibrium had been reached a 600 millicurie radium source S was dropped into the well which offered a snug fit. The yield of cerous ions

TABLE VI

EFFECT OF TEMPERATURE ON THE YIELD OF CEROUS ION

T, °C.	Yield, cerous ions/100 ev.	Error, cerous ions/100 ev.
5.8	3.32	±0.055
22.1	3.25	0.045
37.5	3.095	0.020
53.0	3.04	0.02
73.0	3.02	0.10

was measured at several temperatures. A correction was made for the change in density of the solution, i.e. the electron density, with temperature. The results are recorded in Table VI. The Arrhenius plot gives a negative temperature coefficient, $E = -300$ cal.

In view of the large amount of energy absorbed per ceric ion reduced (ca. 30 ev.) a negative temperature coefficient of 300 cal. activation energy has little

significance for the primary process. At the present state of knowledge it is not possible to assign this energy to a particular process with any degree of certainty.

G. *Effect of Hydrogen Gas*

A solution of ceric ion in 0.8 *N* sulphuric acid solution was deaerated in the apparatus described previously (Fig. 5). After the final thawing, hydrogen gas was introduced to a pressure of 700 mm. through a mercury-sintered glass seal at R. The apparatus was sealed off at J and allowed to stand overnight.

TABLE VII

EFFECT OF HYDROGEN ON THE YIELD

INITIAL CERIC ION CONCENTRATION 1.20×10^{-4} *M*

RATE OF ENERGY ABSORPTION 2.5×10^{-3} EV./SEC./ML.

Pressure H_2, mm.	Concentration H_2, moles/liter	Yield, cerous ions/100 ev.
700	7.0×10^{-4}	6.30 ± 0.3
650	6.5	6.45 ± 0.2
710	7.1	6.50 ± 0.15
700	7.0	6.3 ± 0.20
		Mean 6.4 ± 0.25

Ratio of yields $\frac{H_2 \text{ saturated}}{\text{airfree}} = 1.94 \pm 0.10$

Five milliliter samples were decanted into the side tubes, which were sealed off and irradiated. The solution remaining in A was analyzed for the ceric ion concentration. The whole deaeration process plus hydrogen admission changed the concentration of ceric ion about 1%. The results are compared with the air-free solution yield in Table VII. The yields are obtained from the ratio of the cerous ions produced to energy absorbed.

DISCUSSION

Ceric ion in 0.8 *N* sulphuric acid is certainly not present as the unassociated Ce^{4+} ion. A spectral study showed that it exists as a mixture of $Ce(SO_4)_3^{=}$ (95%) and $Ce(SO_4)_2$(5%) (13). However, for simplicity ceric ion will be written Ce^{4+} in the subsequent discussion, regardless of the degree of association with sulphate ion.

The absorption of ionizing radiation in water has been supposed ordinarily to result in two processes leading to the formation of free radicals, viz. ionization and excitation. The ionization process results in the production of hydrogen and hydroxyl radicals distributed in concentric circles about the ionizing track. The initial radius of the H atom cylinder has been estimated to be 150 Å. while that of the OH radicals is about 8 Å. (19). Radicals produced in this manner will have a relatively long life and will react with any suitable solute present in moderate concentrations. The number of radicals produced by ionization will be proportional to the energy absorbed.

A portion of the energy absorbed will cause excitation of the water molecules. A fraction of these excited water molecules will have sufficient energy to dissociate into hydrogen and hydroxyl radicals. These radicals will be formed in close proximity and, in contrast to radicals formed by ionization, will have a relatively short lifetime.

Radical pairs produced from excited water molecules will usually recombine to form water. At high solute concentrations there is a possibility that reaction might occur between a solute molecule and one of the radicals. This would show up as an increase in yield at high solute concentrations. No such effect has been observed even with 10^{-2} *M* ceric ion, hence any contribution of excited water molecules to the yield has been neglected. Subsequent mention of free radicals will refer only to those produced as a result of the ionizing process along the track.

Oxidizing agents such as ceric ion are attacked by hydrogen atoms

$$Ce^{4+} + H \rightarrow Ce^{3+} + H^{+}. \qquad (1)$$

The yield of cerous ions produced by the reduction of ceric ion has been found independent of ceric and cerous ion concentration over a large range (10^{-2} to 2×10^{-6} moles per liter). Thus either all, or a constant fraction, of the hydrogen atoms produced react with the solute. This concentration independence seems to be typical of the indirect action of ionizing radiation in dilute aqueous solutions. The results with ceric sulphate considerably lower the known lower limits of this concentration independence (cf. Lea (17)). The consequence of these results in terms of the mechanism of free radical formation will be examined subsequently.

Most reactions induced by ionizing radiation are independent of the energy of the incident radiations. For example Weiss (23) has shown the hydroxylation of benzene to be independent of wave length over a wide range. The reduction of ceric ion follows this rule over the small range studied (0.8 to 1.2 Mev.).

Another aspect of indirect action of ionizing radiation is that chemical yield is independent of the rate of energy absorption. There is apparently no lower limit. With different solutes, however, various upper limits have been reported. Miller (18) concludes that the yield of ferric ion from the oxidation of air saturated ferrous sulphate solution falls off above 6×10^{15} ev. per ml. per sec. In biological systems the yield falls off at still lower rates of energy absorption (6). The yield of cerous ion is independent of the rate of energy absorption throughout the range studied. The upper limit must certainly be beyond the value of 3.5×10^{16} ev. per ml. per sec. The significance of this in relation to the primary mechanism will be discussed subsequently.

Oxygen has an effect on the yield of many γ-ray induced reactions. Ferrous ion oxidation is increased (18), formic acid gives different products (11), and biological systems are markedly affected (6). The yield of cerous ion does not vary whether oxygen is initially present or not (cf. Tables I and V).

When oxygen is present as dissolved gas in ceric sulphate solution a competition exists between the two solutes for hydrogen atoms.

$$Ce^{4+} + H \rightarrow Ce^{3+} + H^+ \quad (1)$$

$$O_2 + H \rightarrow HO_2 \quad (2)$$

The relative incidence of Reactions 1 and 2 depends, among other factors, on the relative concentrations of ceric ion and oxygen. The solubility of oxygen gas in equilibrium with air is about 4.5×10^{-4} moles per liter. Whether hydrogen atoms react with oxygen or ceric ion makes no difference to the final yield and products, probably because the reaction

$$Ce^{4+} + HO_2 \rightarrow Ce^{3+} + H^+ + O_2 \quad (3)$$

is very fast. At low ceric concentration reaction (2) may go a step further

$$HO_2 + H \rightarrow H_2O_2. \quad (4)$$

This, however, is followed rapidly by

$$H_2O_2 + Ce^{4+} \rightarrow HO_2 + Ce^{3+} + H^+. \quad (5)$$

It is impossible to have a truly oxygen free system, as oxygen is a product of the reaction. However, the reaction can be studied with such a high ceric ion/oxygen ratio that there is no doubt the ceric ion is reacting with the hydrogen atoms almost exclusively, since results obtained when but little reaction has taken place give the same yield as irradiations in aerated solution.

The reasons for the small negative temperature coefficient for the ceric ion reduction are not at all clear and will not be discussed further. However, such a result eliminates the need for careful temperature control in studying the effect of other variables on the irradiation of ceric sulphate solutions. All other irradiation experiments have been carried out at room temperature (about 22°C.).

The reaction of ceric ion with hydrogen atoms leaves an excess of hydroxyl radicals. Contrary to the ideas of Weiss (21), these do not react with cerous ion. The zero-order kinetics hold to 100% reduction and no reverse reaction occurs. Irradiation of cerous sulphate solutions produces no trace of ceric ion.

REACTION OF HYDROXYL RADICALS

The hydroxyl radicals remaining in the solution after the reaction of ceric ion with the hydrogen atoms must either combine or disproportionate,

$$HO + OH \rightarrow H_2O_2 \quad (6)$$

$$HO + OH \rightarrow H_2O + \tfrac{1}{2} O_2 \quad (7)$$

Weiss (21) has held that Reaction (7) must occur, basing his argument on the dipole attraction of OH radicals favoring this reaction. Reaction (6) is known to occur in the gas phase and there is evidence that it takes place along the tracks of α-particles. The alleged evidence for this reaction in γ-ray induced electron tracks is capable of other interpretations.

This question may be resolved by reference to the ceric ion reduction. Consider Equation (6) and the associated reactions (I)

$$H_2O \rightsquigarrow H + OH \quad \times 2$$
$$H + Ce^{4+} \rightarrow H^+ + Ce^{3+} \quad \times 2$$
$$OH + OH \rightarrow H_2O_2$$
$$H_2O_2 + 2Ce^{4+} \rightarrow 2H^+ + 2Ce^{3+} + O_2$$
$$4Ce^{4+} + 2H_2O \rightarrow 4Ce^{3+} + 4H^+ + O_2$$
$$\frac{\text{Moles } Ce^{4+} \text{ reduced}}{\text{Moles } O_2 \text{ formed}} = 4$$

M/N (ionic yield = number of cerous ions produced per ion pair formed in water) = 2

From Equation (7) and associated reactions (II)

$$H_2O \rightsquigarrow H + OH \quad \times 4$$
$$H + Ce^{4+} \rightarrow H^+ + Ce^{3+} \quad \times 4$$
$$HO + OH \rightarrow H_2O + 1/2\,O_2 \quad \times 2$$
$$4Ce^{4+} + 4H_2O \rightarrow 4H^+ + 4Ce^{3+} + O_2 + 2H_2O$$
$$\frac{\text{Moles } Ce^{4+} \text{ reduced}}{\text{Moles } O_2 \text{ formed}} = 4 \qquad M/N = 1.$$

The yield of 3.30 ions reduced/100 ev. absorbed may be written as 30.3 ev./ion reduced. This value is quite close to the value of 32.5 ev. normally used in the computation of the ion pair yield in pure water. The M/N found by experiment is 1.05. From this it seems likely that the reaction $OH + OH \rightarrow H_2O + 1/2\,O_2$ predominates over any other.

Additional evidence may be obtained if one introduces into the system a substance which will change a hydroxyl radical into a reducing entity. Such a material is dissolved hydrogen gas. The excess hydroxyl radicals will react with hydrogen molecules

$$OH + H_2 \rightarrow H_2O + H. \qquad (8)$$

This conversion of hydroxyl radicals into hydrogen atoms now makes available two reducing atoms per free radical pair.

If Mechanism I is valid, there will not be an increase in the yield of cerous ion on the addition of hydrogen gas to the system, as the OH radical can already reduce ceric ion indirectly through the intermediate hydrogen peroxide. If, on the other hand, Mechanism II is correct, an increase in yield to a maximum of twice the normal value should occur on the introduction of hydrogen gas.

The results in Table VII show that hydrogen gas caused the yield to be doubled. This strongly suggests that the excess OH radicals produced in the reduction of ceric ion form water and oxygen gas directly and do not form hydrogen peroxide. The doubling of the yield indicates that practically all of the OH radicals react with hydrogen.

Further confirmation of this postulate may be obtained from the results of Toulis (19). He measured the amount of hydrogen peroxide produced by the action of X rays on air-free water containing small added amounts of hydrogen and oxygen gases. When the amount of oxygen was kept constant the yield of hydrogen peroxide increased as the amount of hydrogen gas present was increased. This result may be explained by assuming that hydrogen peroxide is formed only by the reaction of hydrogen atoms with oxygen, and not from the combination of two hydroxyl radicals. Increasing the amount of hydrogen gas results in more hydroxyl radicals disappearing by Reaction (8) than by Reaction (7). Thus extra hydrogen atoms produced combine with oxygen to increase the hydrogen peroxide yield.

If one assumes that all hydrogen atoms react with ceric ions, then a calculation of the average energy required to produce a free radical pair may be made. The yield is, within experimental error, doubled by the introduction of hydrogen gas; hence it may be assumed that hydroxyl radicals are completely efficient in their reaction with hydrogen gas. On these assumptions the energy required to produce a free radical pair in water is just 30.3 ev.

The assumption that the ionic yield M/N is about 1 is at variance with the results of Clarke and Coe (3), who found that M/N had a value of 2. We can offer no explanation for this great divergence, as it is certainly outside any experimental error. The only great difference in experimental technique is in the relative energy of the X rays used by Clarke and Coe to the γ-rays used in the present work, viz. 50 kv. compared with 1200 kv. The problem of measuring the energy absorbed is more difficult at longer wave lengths. However, until this work is carried out at lower X-ray energies a comparison of the two sets of results is not strictly permissible.

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RADIATION CHEMISTRY INVESTIGATION OF AQUEOUS SOLUTIONS USING P^{32} AND S^{35} AS INTERNAL SOURCES[1]

By T. J. Hardwick

ABSTRACT

The oxidation of ferrous ion and the reduction of ceric ion in 0.80 *N* sulphuric acid by electrons from dissolved P^{32} and S^{35} have been studied. The chemical yields (chemical change per unit energy absorbed) obtained agree well with those obtained using X or γ-radiation. The yield is independent of electron energy above about 5 kev. The results show that chemical dosimetry methods may be used for the accurate determination of energy absorption for electron energies as low as 45 kev, or X rays of 200 kev.

INTRODUCTION

In recent years there has been increasing interest in the use of chemical dosimeters for the measurement of absorbed energy in a field of ionizing radiation. Several chemical systems have been suggested, e.g., oxidation of air saturated ferrous sulphate solutions (5, 6, 7, 14), decomposition of aqueous chloral solution (2), decoloration of methylene blue (16) in solution. These depend on obtaining an absolute value of the yield (chemical change per unit energy absorbed). The main difficulty in such a measurement is the accurate determination of the amount of energy absorbed. The most reliable determinations of chemical yield have made use of the Bragg–Gray cavity principle, whereby the saturation ion current in an air cavity in a field of radiation can be directly compared with the rate of chemical change of a solution placed in the same cavity in the same radiation field. This method has given satisfactory results with both radium and cobalt 60 sources (10, 14).

These results may be checked in a quite independent manner by using electrons emitted from beta active radioisotopes dissolved in the dosimeter solution as a source of energy. The absorption of X and γ-rays gives rise to fast electrons, the slowing down of which eventually results in chemical changes. Electrons of the same energy produced by these two processes will have identical properties and will produce the same chemical effect. The rate of energy absorption from a dissolved radioisotope may be obtained from a measurement of the disintegration rate and a knowledge of the beta spectrum.

The Bragg–Gray cavity principle requires that no fast electrons originate or terminate in the air filled cavity (8, 17). Thus when the energy of the incident photons is low the range of the primary electrons will be short and the dimensions of the cavity must be correspondingly small. In practice, with photon energies below 500 kev. the dimensions of the cavity become impracticably small. Hence chemical yields for photon energies below 500 kev. have not been directly measured.

This limitation may be overcome by the use of a radioisotope emitting beta particles of low energy. For example, beta particles emitted with an average

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energy of 50 kev. would have the same average energy as electrons produced by the absorption of a 220 kev. X ray (13). Furthermore, the chemical reactions produced by these low energy electrons will correspond to the reactions at the end of the tracks of higher energy electrons. Any variation in the nature of the chemical reactions with varying average electron energy will indicate that a corresponding variation occurs along the track of a single electron as its energy diminishes. Such variations are particularly to be expected at the ends of the tracks, where the ionization density undergoes a sudden increase (1).

The radioisotopes used as internal sources should have the following properties: (1) the beta emission must have no accompanying γ-ray, (2) the absolute amount present in solution must be readily and accurately measurable, (3) they must be capable of incorporation chemically into the system and have no effect on the normal course of the reaction. A knowledge of the average energy per beta particle is essential.

Two appear to satisfy requirements: P^{32} (average energy 697 kev. (3, 18)) and S^{35} (average energy 45.75 kev. (4)), representing high and low energy electrons. The photon energies required to produce electrons of these average energies are ca. 1.45 Mev. and 205 kev. respectively (13). These isotopes, in the form of phosphate and sulphate, were added to the dosimeter solution and the chemical change measured. The concentration of radioisotope chosen was such that the rate of energy absorption was similar to that used in previous dosimetry work (10), ca. 2×10^{13} ev. per ml. per sec.

Two reactions were studied: (1) the oxidation of ferrous ion in 0.80 *N* sulphuric acid solution and (2) the reduction of ceric ion in 0.80 sulphuric acid solution. The first system has already been investigated with a view to its use as a chemical dosimeter (5, 7, 14). The yield has been found to be as 20.8 ions oxidized per 100 ev. absorbed.

No dosimetry studies have heretofore been carried out using ceric sulphate solutions, but this system is known to possess suitable characteristics for a dosimeter (9). The relative yields of the ferrous sulphate system and ceric sulphate systems have been carefully measured using γ-rays from Co^{60} as a source of radiation. The yield in the ceric system is 3.30 cerous ions per 100 ev. absorbed. Previous work with Ra γ-rays and Co^{60} γ-rays has shown that the yield of cerous ion in the ceric sulphate system is independent of both cerous and ceric ion concentration under the conditions used in these experiments (9). Similarly the yield of ferric ion is independent of the concentration of ferrous or ferric ions in the concentrations used (10, 14). A dependence of yield on concentration was not expected with internal sources.

The course of these reactions can conveniently be followed with a spectrophotometer. In 0.80 *N* sulphuric acid, ferric ions absorb strongly in the ultraviolet region 350-300 mμ, where ferrous ions absorb a negligible amount of light. Similarly, ceric ions absorb strongly in the region 380-300 mμ, whereas under these conditions cerous ions do not. The solutions containing the radioactive isotopes were placed in optical cells of a spectrophotometer, and the

change in transmission measured with time. From these rate data, together with a determination of the amount of radioactive material present in solution, the chemical yield may be calculated.

EXPERIMENTAL AND RESULTS

A. *Preparation of Inactive Solutions*

Ferrous sulphate solution was made by dissolving Merck's Reagent Grade ferrous ammonium sulphate in dilute sulphuric acid. The acid used was Nichols' C.P. Grade, and the concentration was such that when mixed with the radioactive solution the final acid concentration was 0.80 *N*. The water used was successively distilled from alkaline permanganate and alkaline manganous hydroxide suspension.

The rate of oxidation of ferrous ion was determined by measuring the rate of production of ferric ion photometrically. The transmission of the solution was measured in a Beckman Quartz Photoelectric Spectrophotometer at wave lengths between 304 and 360 mμ, the wave length selected being such that the percentage transmission was between 20 and 60% (12). With a knowledge of the molar extinction coefficients of ferric ion in 0.80 *N* sulphuric acid in this region of wave length, obtained in a separate experiment, the rate of ferric ion production was measured. Absorption of light by ferrous ion is negligible under these conditions. An excess of oxygen was always present throughout each run. This is known to be necessary in order that the chemical yield shall remain unchanged during the run (14).

Ceric sulphate solution was made by dissolving G. F. Smith Co. ceric ammonium sulphate in dilute sulphuric acid (Nichols' C.P. Grade). The rate of reduction of ceric ion was determined by measuring the change of optical absorption of the solution with time in the wave length range 330-400 mμ. The molar extinction coefficients of ceric ion in 0.80*N* sulphuric acid were determined in a separate experiment. The absorption of light by cerous ion is negligible under these conditions.

B. *Preparation of Isotopes*

P^{32}

Two hundred millicuries of carrier free P^{32} in the form of a phosphoric acid solution was obtained from the Isotope Production Branch.* Ten milliequivalents of sulphuric acid was added, and the solution evaporated to fuming. A small amount of concentrated nitric acid was added and the solution evaporated to sulphuric acid fumes. Repetitions of this evaporation of nitric acid ensured the removal of organic material. The solution was then diluted to 5 ml. giving a stock solution containing 40 mc. per ml. of P^{32} and 2 *N* in sulphuric acid.

Forty-eight milliliters of a solution containing 0.75 *N* sulphuric acid and either ca. 10^{-3} *M* ferrous ion or ca. 10^{-4} ceric ion were mixed with 2 ml. of the P^{32} stock solution and distributed to the optical cells.

**Isotope Production Branch, Chalk River Laboratories, National Research Council of Canada.*

S^{35}

Four hundred millicuries of S^{35} in the form of a sulphuric acid solution was obtained from the Isotopes Production Branch. Five milliequivalents of sulphuric acid was added, and the solution evaporated to sulphuric acid fumes. Organic matter was removed as in the treatment of P^{32} by the addition of nitric acid and subsequent evaporation. The solution was diluted to 1 ml. giving a stock solution containing 400 mc. per ml. of S^{35} in 5 *N* sulphuric acid.

With 9.8 ml. of a solution containing 0.70 *N* sulphuric acid and either ca. 10^{-4} *M* ceric ion or ca. 10^{-3} *M* ferrous ion was mixed 0.200 ml. of the S^{35} stock solution and the mixture was distributed to the optical cells.

C. *Absolute Measurement of the Amount of Radioisotope*

Phosphorus

P^{32} was counted in a 4π geometry counter in the proportional region (11). The absolute error in this measurement is $\pm 1\%$.

Sulphur

S^{35} was determined in two ways: (1) inside a 4π geometry counter in the proportional region, and (2) in an air ion chamber.

The proportional counter measures the rate of beta particle emission. This number, multiplied by the average energy of the beta particles (obtained in this case from the spectrum given by Cockroft (4)) gives the total rate of energy dissipation. The ion current in the ion chamber measures directly the product of the rate of beta particle emission and the average number of ion pairs produced per particle in air. The rate of energy dissipation is calculated by multiplying this result by the energy required to produce an ion pair in air. No detailed knowledge of the beta spectrum is required.

(1) *4π Geometry counter.*—The sulphur sample was evaporated on a thin plastic film and placed in the center of a 4π geometry proportional counter (11). The error in this method of counting is not considered greater than 3% for electrons of this energy.

(2) *Ion chamber measurements.*—A sample of S^{35} was evaporated on a thin aluminum foil (110 μgm. per cm.^{2}) mounted on a wire ring $1\frac{1}{2}$ in. in diameter. This ring, mounted in the center of a spherical ion chamber 8 in. in diameter, was made the collecting electrode. In order that all beta particles be stopped in the chamber, the pressure of air was kept above 2.5 atm. The ion current was measured by following the discharge of the ion chamber by means of a quartz fiber electroscope. Corrections were made for the absorption of beta particles in the aluminum foil. The over-all error in this method is less than 3%.

Calculations for Ion Chamber Measurements

(*a*) Correction due to absorption of energy in foil:

Fraction of energy passing through the foil (15)

$$F = 1 - \frac{x}{R} + \frac{x}{R} \log \frac{x}{R}$$

where x is the foil thickness,

R is the beta particle range in the foil.

But as only half the beta particles are emitted in the direction of the foil, the fraction of the total energy absorbed is $\frac{1+F}{2}$.

The corrected ion current is $I_{corr} = I_{measured} \frac{2}{1+F}$.

(*b*) Determination of rate of energy absorption:

$$\text{Ion current} = \frac{C.V}{T}$$

where C is the capacity of the electroscope,

V is the potential drop in time T

$$\text{Corrected ion current} = \frac{CV}{T}\frac{2}{1+F}.$$

Average energy per ion pair on stopping of a 45.75 kev. electron = 32.4 ev. (17).

$$\text{Rate of energy dissipation} = \frac{CV}{T}\frac{2}{1+F} \times 32.4.$$

This must be multiplied by the dilution factor used in preparing the sample.

D. *Correction for Energy Losses in the Walls*

It was necessary to correct for the fraction of the total energy of the emitted beta particles absorbed in the walls of the vessel. Richards and Rubin (15) have developed a formula for estimating this loss. The correction factor is $\frac{RS}{8V}$ for high energy electrons and $\frac{RS}{6V}$ for low energy electrons, where S/V is the surface/volume ratio of the solution and R is the range of electrons in the medium (taken as the average range in this case). The correction was made to the rate of chemical change: e.g., for P^{32} the corrected rate of chemical change = measured rate of chemical change $\times 1 \Big/ \left(1 - \frac{RS}{8V}\right)$.

With wall losses in mind, the S^{35} work was carried out in 1 cm. Beckman optical cells, while the P^{32} experiments were performed in Beckman 2 cm., 5 cm., and 10 cm. cells concurrently. In this latter case a mean was taken from the corrected rate data.

With 3 ml. of solution in a 1 cm. Beckman cell, the correction for loss of sulphur beta particles was 0.0078. The corrections for P^{32} in solution are shown in Table I.

TABLE I

CORRECTION FOR WALL LOSSES IN BECKMAN CELLS FOR P^{32}

Cell length, cm.	Surface, cm.^{2}	Volume, cm.^{3}	S/V, cm.$^{-1}$	R, cm.	$\frac{RS}{8V}$
2	18.32	6.02	3.043	0.270	.103
5	36.78	15.03	2.447	0.270	.082
10	67.73	30.19	2.243	0.270	.076

E. *Rate Studies*

(1) *Oxidation of Ferrous Ion with* P^{32}

The rate of oxidation of ferrous ion by P^{32} was followed using the three types of optical cells previously mentioned. Corrections to the individual concentration measurements were made for the decay of phosphorus, and to the rate of reaction for the absorption of energy in the cell walls. In Fig. 1 the corrected concentration of ferric ion is plotted against time for the 2 cm. cells; the slope of this line is the rate of the reaction. The mean value for the rate (corrected for wall losses) was $40.7 \pm 0.6 \times 10^{-6}$ moles per liter per hour. The amount of P^{32} present was 4.62×10^{7} dis. per ml. per sec. The yield calculated from these two values was 21.1 ± 0.5 ferric ions per 100 ev. adsorbed.

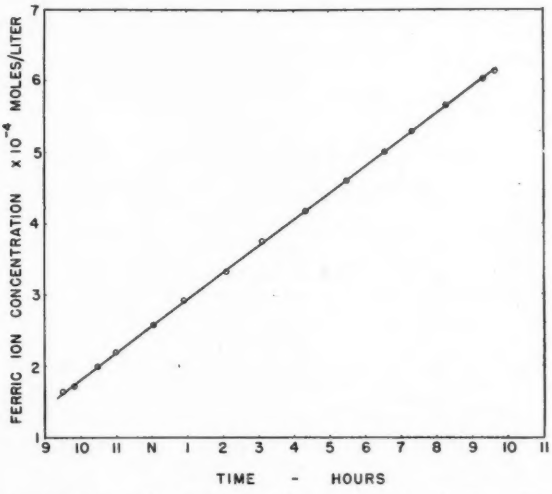

FIG. 1. Production of ferric ion by β^- particles of the P^{32} in solution. These data refer to a 2 cm. cell and are corrected for P^{32} decay.

A similar experiment was carried out using ceric ion instead of ferrous ion, and measuring the rate of reduction. Results were not consistent, probably owing to the adsorption of cerous or ceric phosphate on the glass walls. It was later found that on cleaning the cells, 3 *N* hydrochloric acid removed a relatively large amount of activity from the water washed inner walls.

(2) *Oxidation of Ferrous Ion with* S^{35}

The rate of oxidation of ferrous ion by S^{35} was measured in duplicate in 1 cm. optical cells. Corrections were made for S^{35} decay and absorption of energy in the walls. The mean rate of oxidation of ferrous ion was $18.95 \pm 0.15 \times 10^{-6}$ moles per liter per hour. The amount of S^{35} was 3.05×10^{8} dis. per ml. per sec. as determined by the ion chamber method and 3.04×10^{8} dis. per ml. per sec. as determined by the 4π counter. The yield calculated from these data was 20.2 ± 0.7 ions Fe^{++} oxidized per 100 ev. absorbed.

(3) *Reduction of Ceric Ion with S^{35}*

The rate of reduction of ceric ion by S^{35} was measured in a similar fashion to the oxidation of ferrous ion. The rate of reduction of ceric ion was $2.99 \pm .02 \times 10^{-6}$ moles per liter per hour. The amount of S^{35} measured by the ion chamber method was 3.32×10^{8} dis. per ml. per sec. The yield from these data was $3.32 \pm .08$ ions Ce^{IV} reduced per 100 ev. absorbed.

F. *Sample Calculations: Oxidation of Ferrous Ion by P^{32}*

(All results corrected for radioactive decay)

Mean rate of ferrous ion oxidation $= 40.7 \times 10^{-6}$ moles per liter per hour

(corrected for wall losses) $= 6.81 \times 10^{12}$ ions oxidized per ml. per sec.

Rate of disintegration $= 4.62 \times 10^{7}$ dis. per ml. per sec.

Average energy per disintegration of P^{32} $= 697$ kev.

Average rate of energy of dissipation $= 3.22 \times 10^{13}$ ev. per ml. per sec.

$$\text{Yield} = \frac{6.81 \times 10^{12} \text{ ions oxidized per ml. per sec.}}{3.22 \times 10^{13} \text{ ev. per ml. per sec.}}$$

$$= 21.1 \text{ ions oxidized per 100 ev.}$$

DISCUSSION

The chemical yields measured in these experiments agree very well with those obtained by the cavity technique. Miller (14) and later Hardwick (10) obtained a yield of 20.8 ± 0.3 ferric ions per 100 ev. using the cavity principle. This is to be compared with a yield of 21.1 ± 0.5 ferric ions per 100 ev. using P^{32}.

The yield is independent of the energy of the electrons in the range studied. The yield of cerous ions obtained on irradiation of ceric sulphate in 0.80 *N* sulphuric acid solution with cobalt γ-rays is 3.30 ± 0.06 ions per 100 ev. This agrees very well with the low energy electron results—3.32 ± 0.08 ions per 100 ev. Similarly, with the irradiation of ferrous ion, the results are in good agreement: 21.1 ± 0.5 ferric ions per 100 ev. for P^{32} and 20.2 ± 0.7 ferric ions per 100 ev. for S^{35}.

It has been demonstrated that both ceric sulphate and ferrous sulphate may be used as dosimeters for electron energies as low as 45 kev. This electron energy corresponds to the mean energy produced in water by absorption of a 200 kev. photon. Hence these systems can be used for accurate dosimetry of the X rays from many commercial tubes. In general, the amount of energy absorbed in an irradiated medium has heretofore been determined indirectly by calculations involving several approximations, from measurements made with an air ionization chamber placed in the radiation field.

The independence of yield on electron energy suggests that the primary chemical process occurring in the electron tracks is the same for all energies above 5 kev. Recombination of radicals at the end of electron tracks does not appear to play an important part in chemical reactions. In this connection a

repetition of these experiments using tritium as the radioactive isotope would be quite rewarding.

The results of this paper confirm the correctness of the formulae derived by Richards and Rubin for the corrections arising from termination of electron tracks outside the medium.

ACKNOWLEDGMENTS

The author is indebted to Mr. R. Hawkings for the absolute measurement of P^{32} and S^{35} by counting, and to Dr. H. Carmichael for advice in the measurement of S^{35} by the ion chamber method.

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A THEORETICAL STUDY OF 2,3-DINAPHTHYLENE[1]

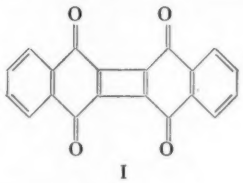
By V. A. Crawford[2]

ABSTRACT

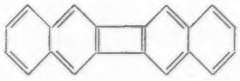
A molecular orbital study of 2,3-dinaphthylene is reported, the molecule being assumed to have a planar structure. The magnitude of the resonance energy shows that the interaction of the π electrons as a whole is quite strongly stabilizing. The bond orders have been computed and from these the lengths of the bonds in the molecule have been deduced. The longest wave length in an allowed excitation probably arises from a transition between mobile electron levels of symmetry $A_{1g} \rightarrow B_{1u}$ and polarized in the direction of the long axis of the molecule.

INTRODUCTION

On account of the cyclobutadiene structure which it contains, *o*-diphenylene has been much studied in the past, whereas the related dinaphthylenes on the other hand have received only scanty attention. Rosenhauer *et al.* (7) starting from α-naphthaquinone obtained a compound to which they assigned the structure I and from this by distillation with zinc dust claimed to have obtained a hydrocarbon which was formulated as II.



I



II

More recently Bell and Hunter (1) distilled I with zinc dust under a variety of conditions but failed to obtain II.

It is the purpose of this communication to record the results of theoretical calculations of the resonance energy, bond orders, and light absorption of 2,3-dinaphthylene in the hope that they may stimulate experimental work with which to compare them.

CALCULATION

The method of calculation, that of molecular orbitals, is well known and need not therefore be described in detail. The electronic wave function of the π electrons is expressed as a linear combination of atomic orbitals and the secular equation found in the usual way (5) and solved subject to the following restrictions.

(i) All the coulomb integrals are assumed to be equal and set equal to α.

(ii) All resonance integrals β_{ij} between the π electrons on adjacent atoms are taken to be identical and set equal to β whereas all other resonance integrals are neglected.

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Contribution from the Wheatstone Physics Laboratory, University of London King's College, London, England, and the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N. R. C. No. 2608.

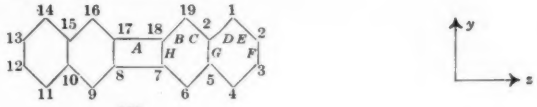
[2] *National Research Council of Canada Postdoctorate Fellow.*

The secular determinant, however, may be factorized for the symmetry elements of the molecule belong to the point group D_{2h}. The 20 $2p_x$ atomic orbitals $\phi_i (i = 1, \ldots, 20)$ (see below) constitute a reducible representation Γ of this point group and it may readily be shown to have irreducible components

$$\Gamma = 5B_{3u} + 5B_{2g} + 5B_{1g} + 5A_{1u}$$

For group theoretical details see Eyring, Walter, and Kimball (3).

The *LCAO* forms of the molecular orbitals are



III

$$\psi(B_{3u}) = c_1(\phi_{18} + \phi_7 + \phi_{17} + \phi_8) + c_2(\phi_{19} + \phi_6 + \phi_{16} + \phi_9) + c_3(\phi_{20} + \phi_5 + \phi_{15} + \phi_{10}) + c_4(\phi_1 + \phi_4 + \phi_{14} + \phi_{11}) + c_5(\phi_2 + \phi_3 + \phi_{13} + \phi_{12})$$

$$\psi(B_{2g}) = c_1'(\phi_{18} + \phi_7 - \phi_{17} - \phi_8) + c_2'(\phi_{19} + \phi_6 - \phi_{16} - \phi_9) + c_3'(\phi_{20} + \phi_5 - \phi_{15} - \phi_{10}) + c_4'(\phi_1 + \phi_4 - \phi_{14} - \phi_{11}) + c_5'(\phi_2 + \phi_3 - \phi_{13} - \phi_{12})$$

$$\psi(B_{1g}) = c_1''(\phi_{18} - \phi_7 + \phi_{17} - \phi_8) + c_2''(\phi_{19} - \phi_6 + \phi_{16} - \phi_9) + c_3''(\phi_{20} - \phi_5 + \phi_{15} - \phi_{10}) + c_4''(\phi_1 - \phi_4 + \phi_{14} - \phi_{11}) + c_5''(\phi_2 - \phi_3 + \phi_{13} - \phi_{12})$$

$$\psi(A_{1u}) = c_1'''(\phi_{18} - \phi_7 - \phi_{17} + \phi_{18}) + c_2'''(\phi_{19} - \phi_6 - \phi_{16} + \phi_9) + c_3'''(\phi_{20} - \phi_5 - \phi_{15} + \phi_{10}) + c_4'''(\phi_1 - \phi_4 - \phi_{14} + \phi_{11}) + c_5'''(\phi_2 - \phi_3 - \phi_{13} + \phi_{12})$$

From the roots of the secular equation the coefficients c_i are calculated and each molecular orbital normalized.

RESULTS

Resonance energy: The total energy E^{mobile} of the molecule in its ground state is found to be $20\alpha + 27.980\beta$. Since the total energy of the π electrons in a localized bond structure is $20\alpha + 20\beta$ the resonance energy is 7.980β. That is, the molecule should have a considerable resonance energy, the value per π electron being slightly greater than that of benzene.

Bond order: This is defined by $p_{rs} = 2\,\Sigma c_r c_s$ (2), the summation being over the 10 molecular orbitals of lowest energy since the molecule has altogether 20 π electrons. Summing over these orbitals yields the bond orders given in Table I.

The bond lengths corresponding to the partial mobile bond orders were read off from a graph of bond length against bond order, this curve being defined by the data recorded in Table II.

TABLE I

PARTIAL MOBILE BOND ORDERS AND BOND LENGTHS IN 2,3-DINAPHTHYLENE

Bond	Mobile order	Bond length (*A*)
A	0.316	1.464
B	0.722	1.387
C	0.529	1.422
D	0.570	1.415
E	0.711	1.389
F	0.614	1.407
G	0.520	1.424
H	0.485	1.431

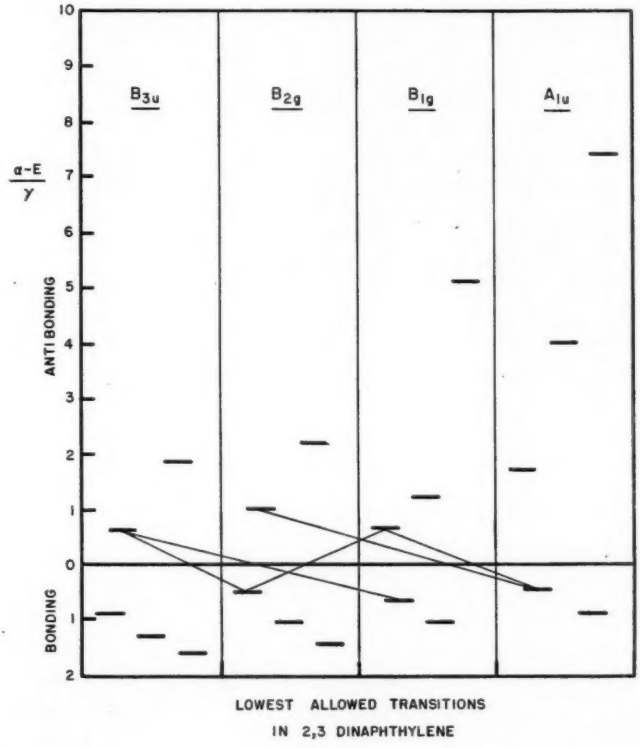


FIG. 1

TABLE II

Molecule	Mobile order	Bond length
Ethane	0	1.541
Graphite	0.525 (Ref. 2)	1.421 (Ref. 6)
Ethylene	1	1.340 (Refs. 4, 8)

The third decimals of the bond length values of Table I are useful for comparative purposes but are not reliable absolutely. Notice that bonds B and E are predicted to have the same length of approximately 1.39 A and also that bonds C and G are equal, with lengths of about 1.42 A.

Spectra: In the ground state of the molecule the mobile electrons occupy in pairs all the bonding orbitals, the ground state description being,

$$(b_{3u})^2(b_{2g})^2(b_{3u})^2(b_{2g})^2(b_{1g})^2(a_{1u})^2(b_{3u})^2(b_{1g})^2(b_{2g})^2(a_{1u})^2,$$

electrons of greatest binding energy coming first.

To determine the excitation energies the orbital energies are first corrected for overlap using $S = 0.25$ (9) the corrected energies in units of $(\alpha - E)/\gamma$ being shown in Fig. 1. Here γ is a new resonance integral which replaces β and is equal to $\beta - \alpha S$. The solid line corresponds to $E = \alpha$ and the orbitals below this line are bonding, those above it antibonding.

Different excited states are obtained by taking an electron from a bonding orbital and placing it in an antibonding one. The first excited state corresponds to the transition from the highest bonding orbital (N) to the lowest antibonding one (V_1) the corresponding excitation energy determining the longest

TABLE III

$N \rightarrow V$ TRANSITIONS IN 2,3-DINAPHTHYLENE

Transition	Excited configuration	Polarization	Calculated transition energy	
			γ	Cm.$^{-1}$
$N \rightarrow V_1$	B_{1u}	z	1.079	24,800
$N \rightarrow V_2$	B_{1u}	z	1.101	25,300
$N \rightarrow V_3$	B_{3g}	Forbidden	1.131	26,000
$N \rightarrow V_4$	B_{2u}	y	1.260	29,000
$N \rightarrow V_5$	A_{1g}	Forbidden	1.312	30,200
$N \rightarrow V_6$	B_{2u}	y	1.459	33,600

wave length absorption. This is an allowed transition with polarization along the z axis. Other allowed transitions are possible and some of these together with their polarizations are shown in Table III.

The transition energy in cm.$^{-1}$ was obtained by assigning to γ a value of 23,000 cm.$^{-1}$ Since on excitation the electron spins may be parallel the transition energies listed above really give the location of the centers of gravity of singlet–triplet pairs in the spectrum.

Excitation is confined to either the B_{1u} or B_{2u} configurations for the ground state of the molecule is A_{1g} and allowed transitions must satisfy the $g \leftrightarrow u$ selection rule. Interaction between the lowest B_{1u} states will cause a slight lowering of the $N \rightarrow V_1$ transition energy and in like manner interaction between the β_{2u} states will lower the $N \rightarrow V_4$ energy. It is not expected, however, that this will invert the B_{1u} and B_{2u} levels so that the lowest allowed transition might be anticipated to be polarized in the z direction.

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STUDY OF 4-MONO- AND 4,4-DISUBSTITUTED-3-IMINO-2-BENZOYL-5-PYRAZOLONES[1]

By Paul E. Gagnon, Jean L. Boivin,[2] Paul A. Boivin,[3] and Hugh M. Craig[4]

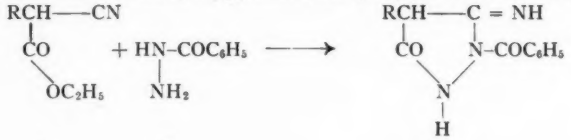
ABSTRACT

4-Mono- and 4,4-disubstituted-3-imino-2-benzoyl-5-pyrazolones have been prepared from the corresponding ethyl mono- or disubstituted cyanoacetates and N-benzoylhydrazine. The presence of the imino group in 4, 4-disubstituted-3-imino-2-benzoyl-5-pyrazolones was ascertained by the hydrolysis of 4, 4-dibenzyl-3-imino-2-benzoyl-5-pyrazolone into 4, 4-dibenzyl-3-oxo-2-benzoyl-5-pyrazolone. In order to prove that the benzoyl group in these pyrazolones was not in Position 1, the synthesis of 4-benzyl-3-amino-1-benzoyl-5-pyrazolone was attempted from 4-benzyl-3-carbethoxy-1-benzoyl-5-pyrazolone through a Curtius degradation of the 3-carbethoxy substituent into a 3-amino group. It was found that the 1-benzoyl group was hydrolyzed at the same time as the 3-carbethoxyamino substituent. The ultraviolet absorption spectra of all these compounds are reported and discussed briefly.

INTRODUCTION

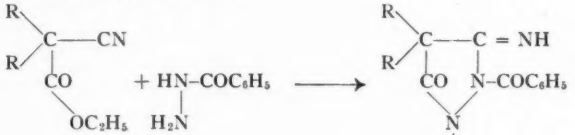
Pyrazolones prepared from ethyl mono- or disubstituted cyanoacetates and hydrazine have been previously reported (1,3). Phenylhydrazine and semicarbazide were condensed in the same way to yield the corresponding 2-phenyl (1) and 2-carboxamido-5-pyrazolones (2).

It was thought of interest to study the condensation of N-benzoylhydrazine under similar conditions. By reacting ethyl monosubstituted cyanoacetates (I) with N-benzoylhydrazine (II) in the presence of sodium ethylate, 4-monosubstituted-3-imino-2-benzoyl-5-pyrazolones (III) were obtained (Table I).



I II III

The reaction of ethyl disubstituted cyanoacetates (IV) with N-benzoylhydrazine under similar conditions yielded 4,4-disubstituted-3-imino-2-benzoyl-5-pyrazolones (V) (Table II).



IV V

[1] *Manuscript received in original form February 26, 1951, and as revised, October 16, 1951. Contribution from the Department of Chemistry, Laval University, Quebec, Que. This paper constitutes part of a thesis submitted to the Graduate School in partial fulfilment of the requirements for the degree of Doctor of Science.*

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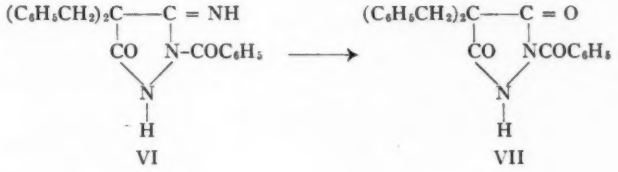
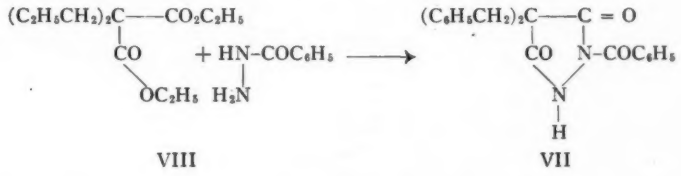
The presence of an imino group in the 4, 4-disubstituted-3-imino-2-benzoyl-5-pyrazolones was demonstrated by the hydrolysis of 4,4-dibenzyl-3-imino-2-benzoyl-5-pyrazolone (VI) into 4, 4-dibenzyl-3-oxo-2-benzoyl-5-pyrazolone (VII).



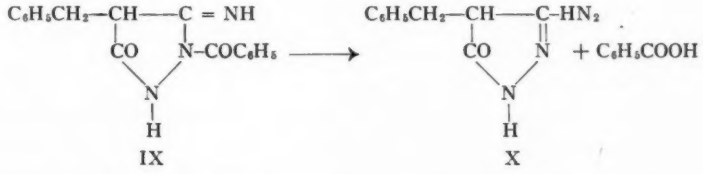
VI VII

Several hydrolyzing agents were found to remove the imino group along with benzoyl substituent. However, by using 2 *N* sulphuric acid, only the imino group was hydrolyzed. Compound VI was converted, although not quantitatively, into pyrazolone VII, which was proved to be identical with the substance prepared from ethyl dibenzylmalonate (VIII) and N-benzoyl-hydrazine.



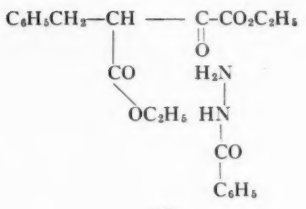
VIII VII

The ease with which the benzoyl group of these pyrazolones was removed has served to prove the cyclic structure of these compounds. By refluxing 4-benzyl-3-imino-2-benzoyl-5-pyrazolone (IX) in alkaline solution, 4-benzyl-3-amino-5-pyrazolone (X) and benzoic acid were obtained.

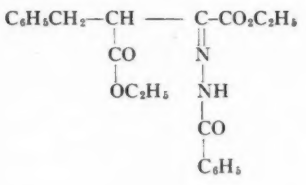


IX X

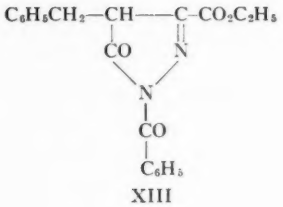
Since there is evidence that these substances contained an imino group and are of cyclic structure, it was thought that an unequivocal synthesis of a benzoylpyrazolone would establish the position of the benzoyl substituent. Although the proof has been made that the phenyl group of 3-amino-1-phenyl-5-pyrazolone (5) is in 1-position and that of 4-benzyl-3-amino-2-phenyl-5-pyrazolone (2) in 2-position, there was no certainty about the position of the benzoyl group in the benzoylpyrazolones. The synthesis of 4-benzyl-3-amino-1-benzoyl-5-pyrazolone (XVII) was attempted through the following scheme:



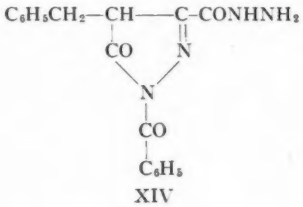
XI



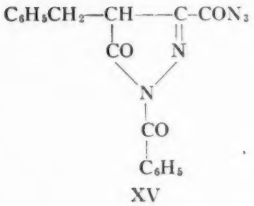
XII



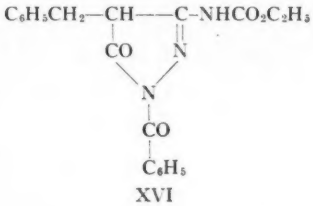
XIII



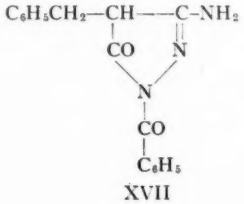
XIV



XV



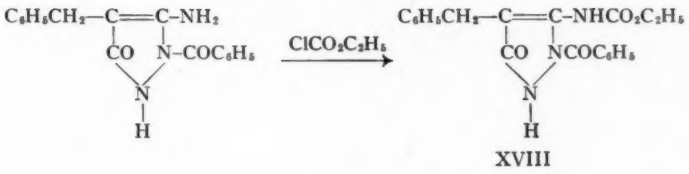
XVI



XVII

Ethyl benzyloxalacetate (XI) was reacted with N-benzoylhydrazine to yield the corresponding hydrazone (XII) which upon heating was transformed into pyrazolone XIII. The Curtius degradation of the 3-carbethoxy group of Compound XIII was made through the hydrazide (XIV), azide (XV), and urethane (XVI). The hydrolysis of Compound XVI should have yielded 4-benzyl-3-amino-1-benzoyl-5-pyrazolone (XVII). Attempts to convert the urethane (XVI) into the corresponding 3-amino compound were unsuccessful. In most cases 4-benzyl-3-amino-5-pyrazolone was isolated (1).

Another proof of the position of the benzoyl group 3-imino-2-benzoyl-5-pyrazolones was attempted by reacting these compounds with ethyl chloroformate. No reaction took place.



XVIII

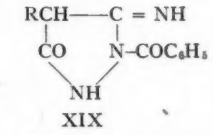
Had an amino group been present, it would have reacted with ethyl chloroformate to yield the corresponding urethane (XVIII) which could have been compared with pyrazolone XVI (5).

Ultraviolet Absorption Spectra

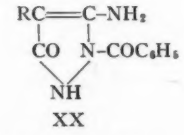
The ultraviolet absorption spectra of the benzoylpyrazolones were determined in neutral, alkaline, and acid solution (1). As can be seen in Tables I and II, the spectra of 4-mono- and 4, 4-disubstituted-3-imino-2-benzoyl-5-pyrazolones are nearly identical in acid and neutral solutions. The maximum absorption wave lengths are the same (2300 Å.) with an intensity of about 4.4 (log E_m). However, in alkaline solution, the curves are quite different. Two maxima are obtained, one at short wave length (2240 Å.) and another one at 3200 Å. of nearly identical intensity (log E_m: 4.2-4.4).

Discussion

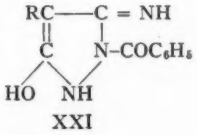
Several tautomeric structures may be possible for the 4-mono-substituted-3-imino-2-benzoyl-5-pyrazolones. Only the following will be considered (XIX-XXII).



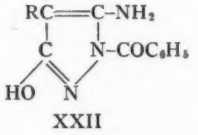
XIX



XX



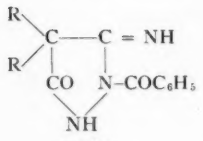
XXI



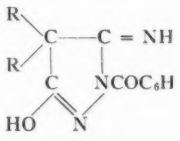
XXII

Since these pyrazolones are soluble in alkaline solution, there is no doubt that Structures XXI and XXII may exist. However, they failed to give a positive color test with ferric chloride indicative of a partial phenolic structure. Moreover, the absence of shift in the ultraviolet absorption spectra in acid medium suggests that an amino group is not present in Position 3 (1). For these reasons, Structure XIX would best represent 4-monosubstituted-3-imino-2-benzoyl-5-pyrazolones.

In the case of 4,4-disubstituted-3-imino-2-benzoyl-5-pyrazolones, the following tautomeric structures may be possible (XXIII and XXIV).



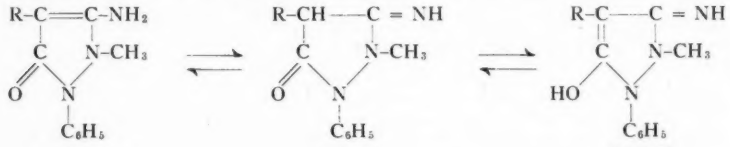
XXIII



XXIV

There is evidence that in alkaline solution as in the case of the monosubstituted derivatives, Structure XXIV may be present. However, in neutral solution, Structure XXIII is the most plausible to represent 4, 4-disubstituted-3-imino-2-benzoyl-5-pyrazolones, since they do not give a positive ferric chloride test. The presence of an imino group was established by hydrolysis. The similarity of spectra in acid and neutral solutions also indicates that they contained an imino group. There is no spectral shift, as usually encountered with aminopyrazolones (2). Therefore, 4-mono and 4,4-disubstituted-2-benzoyl-5-pyrazolones are best represented with an imino group in Position 3.

It is of interest to note that Stenzl and coworkers (4) made studies on methylphenylpyrazolones having the possible structures (XXV-XXVII).

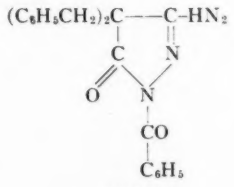


XXV XXVI XXVII

Their conclusions, from a consideration of the chemical properties, were that the most probable structure was XXVI or an equilibrium between XXV and XXVI where XXV appeared only in small amounts.

The position of the benzoyl group was not rigorously demonstrated by the synthesis outlined above, since 4-benzyl-3-amino-1-benzoyl-5-pyrazolone was not obtained, but it can be deduced otherwise.

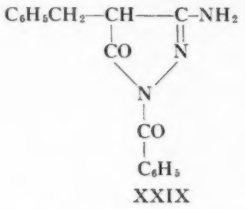
If it is assumed that 4,4-dibenzyl-3-amino-1-benzoyl-5-pyrazolone has Structure XXVIII, this compound



XXVIII

would be insoluble in alkaline solution and would give a spectral shift in acid solution due to an amino group present in Position 3. Since the compound prepared is soluble in alkaline solution and insoluble in active acids, and no spectral shift is obtained in acid medium, Structure XXVIII is unacceptable.

The structure of 4-monosubstituted-3-imino-2-benzoyl-5-pyrazolones is less evident. If the compounds are 1-benzoylpyrazolones,



XXIX

the chemical properties would be partly in accord with Structure XXIX; the solubility in alkaline solution would be explained, but not the insolubility in acid solution and the absence of spectral shift in acid medium.

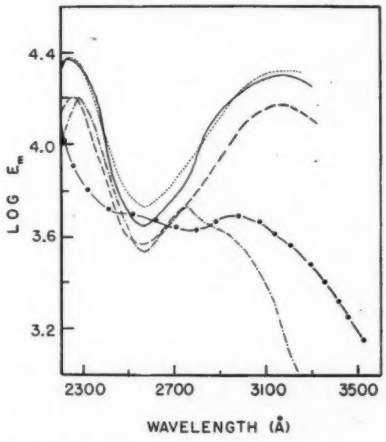
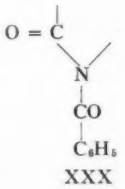


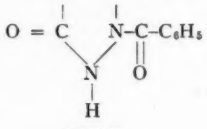
FIG. 1. Ultraviolet absorption spectra.
..... 4, 4-Diamyl-3-imino-2-benzoyl-5-pyrazolone (0.01 *N* sodium hydroxide in ethanol).
———— 4-Amyl-3-imino-2-benzoyl-5-pyrazolone (0.01 *N* sodium hydroxide in ethanol).
— — — — — Dibenzoylhydrazine (0.01 *N* sodium hydroxide in ethanol).
— - — - — Dibenzamide (0.01 *N* sodium hydroxide in ethanol).
— · — · — · 4-Benzyl-3-carbethoxyamino-1-benzoyl-5-pyrazolone (0.01 *N* sodium hydroxide in ethanol).

Alternatively, if it is assumed that Structures XXVIII and XXIX are true, the partial structure XXX



XXX

would be present in both the 4-mono- and 4,4-disubstituted-1-benzoyl-pyrazolones. A comparison of the spectra of dibenzamide with those of 4-amyl-3-imino-2-benzoyl-5-pyrazolone and 4,4-diamyl-3-imino-2-benzyl-5-pyrazolone as determined in the same alkaline solution shows that the spectra obtained differ by the positions of the maxima and their intensities (Fig. 1). If the benzoyl group is in Position 2, the partial structure XXXI



XXXI

would be present in both 4-mono- and 4, 4-disubstituted pyrazolones. The spectrum of N, N′-dibenzoylhydrazine was determined in alkaline solution and was found to be similar in shape and intensity to the spectra of 4-mono- and 4,4-disubstituted-3-imino-2-benzoyl-5-pyrazolones (Fig. 1). Moreover, the spectrum 4-benzyl-3-carbethoxyamino-1-benzoyl-5-pyrazolone (XVI), made by an unequivocal synthesis, shows great difference with that of 2-benzoylpyrazolones.

EXPERIMENTAL*

4-Monosubstituted-3-imino-2-benzoyl-5-pyrazolones (III)

A mixture of ethyl monosubstituted cyanoacetate (0.1 mole) and N-benzoylhydrazine (0.1 mole) was added to a solution of sodium (0.2 mole) in absolute ethanol (80 ml.). After refluxing the mixture for 24 hr., the alcohol was evaporated under reduced pressure and the residue dissolved in water (500 ml.). The solution was extracted with ether to remove unreacted starting materials and the aqueous layer was neutralized with acetic acid (50%). A precipitate was formed. It was filtered and washed with dilute sodium carbonate and water. The solid was crystallized several times from ethanol.

The 4-monosubstituted-3-imino-2-benzoyl-5-pyrazolones prepared were soluble in alkaline solutions and insoluble in active acids. They failed to give a color test with ferric chloride. They are listed, together with their melting points, analyses, and ultraviolet spectrophotometric data in Table I.

4,4-Disubstituted-3-imino-2-benzoyl-5-pyrazolones (V)

These pyrazolones were prepared in the same way as above, except that the ethyl monosubstituted cyanoacetates used were replaced by ethyl disubstituted cyanoacetates.

The 4,4-disubstituted-3-imino-2-benzoyl-5-pyrazolones obtained are listed together with their melting points, analyses, and ultraviolet spectrophotometric data in Table II.

The properties of these pyrazolones are similar to those of the 4-monosubstituted derivatives.

* *All melting points are uncorrected.*

TABLE I

4-MONOSUBSTITUTED-3-IMINO-2-BENZOYL-5-PYRAZOLONES (III)

R	M.p.,°C.	Formula	Analysis, %		Ultraviolet absorption maxima					
			Nitrogen		Neutral		Acid		Alkaline	
			Calc.	Found	Å.	log E_m	Å.	log E_m	Å.	log E_m
C_3H_7	234–236	$C_{13}H_{15}O_2N_3$	17.1	16.9	2300	4.31	2300	4.17	2240 3200	4.31 4.20
C_4H_9	232–233	$C_{14}H_{17}O_2N_3$	16.2	15.9	2300	4.41	2300	4.41	2240 3200	4.31 4.19
C_5H_{11}	233–234	$C_{15}H_{19}O_2N_3$	15.4	15.1	2300	4.39	2300	4.40	2240 3200	4.32 4.23
C_6H_{13}	235–237	$C_{16}H_{21}O_2N_3$	14.6	14.3	2300	4.44	2300	4.46	2240 3200	4.38 4.28
C_7H_{15}	234–235	$C_{17}H_{23}O_2N_3$	13.9	14.0	2300	4.41	2300	4.45	2240 3200	4.37 4.30
C_8H_{17}	236–238	$C_{18}H_{25}O_2N_3$	13.3	13.0	2300	4.48	2300	4.35	2240 3200	4.36 4.29
$C_6H_5CH_2$*	236–237	$C_{17}H_{15}O_2N_3$	14.3	14.0	2300	4.43	2300	4.47	2240 3200	4.32 4.23

* *Calc. for* $C_{17}H_{15}O_2N_3$: *C, 69.6%; H, 5.12%. Found: C, 69.3%; H, 5.22%.*

4,4-Dibenzyl-3-oxo-2-benzoyl-5-pyrazolone (VII)

(*a*) Using the same procedure as outlined for 4-monosubstituted-3-imino-2-benzoyl-5-pyrazolones, Compound VII was obtained from ethyl dibenzylmalonate and N-benzoylhydrazine. This compound melted at 301-302°C. Calc. for $C_{24}H_{20}O_3N_2$: N, 7.29%. Found: N, 7.40%.

(*b*) 4,4-Dibenzyl-3-imino-2-benzoyl-5-pyrazolone (3.8 gm., 0.01 mole) was heated in 2*N* sulphuric acid (50 ml.) for two hours on a steam bath. After cooling, the mixture was filtered and the filtrate evaporated to small volume.

TABLE II

4,4-DISUBSTITUTED-3-IMINO-2-BENZOYL-5-PYRAZOLONES (V)

R	M.p.,°C.	Formula	Analysis, %		Ultraviolet absorption maxima					
			Nitrogen		Neutral		Acid		Alkaline	
			Calc.	Found	Å.	log E_m	Å.	log E_m	Å.	log E_m
$(C_3H_7)_2$	236–237	$C_{16}H_{21}O_2N_3$	14.6	14.5	2300	4.37	2300	4.46	2240 3200	4.32 4.23
$(C_4H_9)_2$	235–236	$C_{18}H_{25}O_2N_3$	13.3	13.0	2300	4.52	2300	4.54	2240 3200	4.39 4.33
$(C_5H_{11})_2$	236–237	$C_{22}H_{29}O_2N_3$	12.2	12.4	2300	4.47	2300	4.40	2240 3200	4.37 4.32
$(C_6H_{13})_2$	236–237	$C_{22}H_{33}O_2N_3$	11.3	11.3	2300	4.40	2300	4.44	2240 3200	4.38 4.25
$(C_7H_{15})_2$	237–239	$C_{24}H_{37}O_2N_3$	10.5	10.5	2300	4.44	2300	4.50	2240 3200	4.59 4.41
$(C_6H_5CH_2)_2$	238–240	$C_{24}H_{21}O_2N_3$	10.9	10.6	2300	4.53	2300	4.58	2240 3200	4.49 4.39

A crystalline product was obtained. Recrystallizations from a water–ethanol mixture gave a compound melting at 301-302°C. A mixed melting point determination with 4,4-dibenzyl-3-oxo-2-benzoyl-5-pyrazolone (VII) was not depressed.

Hydrolysis of 4-benzyl-3-imino-2-benzoyl-5-pyrazolone (IX) into 4-Benzyl-3-amino-5-pyrazolone (X) and Benzoic Acid

4-Benzyl-3-imino-2-benzoyl-5-pyrazolone (15 gm.) was refluxed in 2% aqueous medium hydroxide (300 ml.) for 24 hr. The solution was cooled and acidified to pH 5 with acetic acid (50%). There was precipitation of the unreacted pyrazolone. The filtrate was acidified with concentrated hydrochloric acid to pH 2. Benzoic acid was filtered off and the filtrate was evaporated to dryness and extracted with warm ether to remove all remaining benzoic acid. The solid was heated at 100°C. and 20 mm. pressure to remove all traces of hydrochloric acid. The residue was dissolved in a dilute solution of sodium hydroxide and neutralized with acetic acid. It was evaporated to dryness under reduced pressure and then refluxed with absolute ethanol and filtered. The filtrate was evaporated to dryness and dissolved in hot water. On cooling, white crystals appeared; m.p. 202°C. A mixed melting point with 4-benzyl-3-amino-5-pyrazolone was not depressed.

4-Benzyl-3-carbethoxy-1-benzoyl-5-pyrazolone (XIII)

The ethyl ester of benzyloxalacetic acid (28 gm., 0.1 mole) was heated with N-benzoylhydrazine (13.6 gm., 0.1 mole) at 110°C. for one hour, to give rise to the corresponding hydrazone; the temperature was slowly raised to 190°C. and maintained for three hours. Ethanol was evolved. On cooling, solidification took place. The 1-benzoyl-3-carbethoxy-4-benzyl-5-pyrazolone (32 gm.) was crystallized from ethanol, m.p. 217°C. Calc. for $C_{20}H_{18}O_4N_2$: N, 8.00%. Found: N, 7.86%.

4-Benzyl-3-carboxyhydrazide-1-benzoyl-5-pyrazolone (XIV)

4-Benzyl-3-carbethoxy-1-benzoyl-5-pyrazolone (8 gm., 0.02 mole) was added in small portions to boiling hydrazine hydrate (10 gm., 0.2 mole) and refluxed for five hours. The excess hydrazine was removed under reduced pressure, leaving a resinous material. On addition of hot ethanol (200 ml.) the material dissolved and on cooling crystallized as a white solid (m.p. 203-204°C.). Yield, 6 gm. Calc. for $C_{18}H_{16}O_3N_4$: N, 16.6%. Found: N, 17.0%.

4-Benzyl-3-carboxazide-1-benzoyl-5-pyrazolone (XV)

The hydrazide, XIV (3 gm., 0.01 mole), was dissolved in aqueous hydrochloric acid (20%), and a solution of sodium nitrite (10 gm.) in water (30 ml.) was added in a rapid stream at 0°C. The azide appeared immediately and on completion of the addition the solid was filtered, washed with ice-cold water, and dried on a porous plate, m.p. 135-137°C. (with deflagration). Yield, 3 gm.

4-Benzyl-3-carbethoxyamino-1-benzoyl-5-pyrazolone (XVI)

The azide, XV (3 gm., 0.01 mole), was refluxed in ethanol (20 ml.) and xylene (350 ml.) for one hour. There was evolution of nitrogen. The solution was allowed to stand overnight and crystallization took place. The compound melted at 160-162°C. Calc. for $C_{20}H_{19}O_4N_3$: N, 11.5%. Found: N, 11.6%.

By effecting the hydrolysis of Compound XVI in alkaline solution and working out the materials as in the hydrolysis of 4-benzyl-3-imino-2-benzoyl-5-pyrazolone described above, it was found that Compound XVI was transformed into 4-benzyl-3-amino-5-pyrazolone.

Attempted Synthesis of 4-Benzyl-3-carbethoxyamino-2-benzoyl-5-pyrazolone (XVI)

4-Benzyl-3-imino-2-benzoyl-5-pyrazolone (3 gm.) was added to a solution of ethyl chloroformate (4 gm.) in dioxane (35 ml.). The mixture was heated on a steam-bath for four hours, cooled, and filtered. The filtrate was diluted with water and an amorphous material precipitated out. This product was crystallized from ethanol, m.p. 236-237°C. A mixed melting point determination with the starting material showed no depression.

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MECHANISM OF GUANIDINE NITRATION

I. AZO-*BIS*-NITROFORMAMIDINE[1]

By George F Wright

ABSTRACT

Although azo-*bis*-formamidine dinitrate cannot be converted to the dinitro derivative directly it can be chlorinated in water to azo-*bis*-chloroformamidine and thence to azo-*bis*-nitroformamidine in nitric acid and acetic anhydride. When the latter substance is treated with 2-methylpentadiene-1,3 an alkali-soluble compound is obtained which is specified as 1-imino-3-nitrimino-4,6(or 5,7)-dimethyl-2,8,9-triaza-4,6,8,9-tetrahydroindandione-1,3. The characteristics of this reaction indicate that azo-*bis*-nitroformamidine exists as the nitrimino tautomer. The Diels-Alder reaction with 2-methylpentadiene-1,3 has its counterpart in the similar reaction whereby azo-*bis*-formamidine is converted to 1,3-diimino-4,6-dimethyl-2,8,9-triaza-4,6,8,9-tetrahydroindandione-1,3 mononitrate and ammonium nitrate. The entire sequence of reactions is offered as evidence that the imino group in guanidines is the site of nitration, and its chemistry of nitration is analogous with that of aliphatic secondary amines.

The nitration of aliphatic secondary amides and of primary and secondary aliphatic amines (1,3-5,6,8,12,13,15) has been studied extensively and some understanding of the reaction is now at hand. Firstly it has been found that the ease of nitration in acetic anhydride varies inversely in respect of increasing base strength. Secondly those strong amines which cannot be nitrated directly can be converted to their nitramines via the intermediate preparation of the chloramines, presumably because the chlorine substituent reduces the base strength of the amine. In many cases the chloramine may be prepared *in situ* in the acetic anhydride – nitric acid medium by adding a small amount of hydrogen chloride. The hypochlorous acid thus produced forms the chloramine and is regenerated when the chloramine is converted to the nitramine. A chain reaction is thus developed which is largely self-sustaining. Finally primary amines, which cannot be nitrated directly, may be converted to primary nitramines via the primary dichloramine.

The alkylchloronitramine (which can be converted separately to the alkylnitramine) is the actual product of the latter reaction. This is fortunate because primary nitramines decompose in nitration media, often violently, in strong sulphuric or nitric acid. In acetic anhydride or acetic acid the decomposition rate is dependent on the amount of excess nitric acid which is present.

This instability of primary nitramines toward mineral acid undoubtedly accounts for the fact that acyl primary nitramines are not ordinarily prepared from acid amides. An exception is the conversion of urea nitrate to nitrourea in sulphuric acid, but careful attention to short time and low temperature of reaction must be observed in order to avoid extensive decomposition of the nitrourea. As might have been expected, it has now been found that this decomposition does not occur when nitrourea is formed from urea nitrate in acetic anhydride.

[1] *Manuscript received in original form January 5, 1951, and, as revised, November 27, 1951. Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont.*

In contrast, guanidine nitrate may be converted to nitroguanidine in nitric acid or sulphuric acid without special attention to time and temperature of the reaction medium. It is difficult to reconcile this behavior with that of a primary amido group. Thus the stabilization of a primary nitramino group in nitroguanidine by salt formation with an amino group in the same molecule is a doubtful explanation. The nitramino group in β-aminoethylnitramine (which is typically a zwitterion of this type (10)) is decomposed easily by nitric and sulphuric acid. The stability of a primary nitramino group in nitroguanidine is therefore unique and anomolous.

However recent work has suggested the possibility that nitroguanidine contains a nitrimino rather than a nitramino group (2). This possibility is substantiated by the observation that nitroguanidine does not exhibit acidic behavior in contact with diazomethane. If the nitro group is situated on the imino nitrogen of a guanidine nucleus then it may have been attached at that 2-position during nitration. This hypothesis, which clarifies the previous anomoly respecting stability of many nitroguanidines in the nitration media, indicates a chemical similarity between *imino* and secondary *amino* groups in their behaviors toward nitration media.

Such chemical similarity seems to exist in respect of base strength. Thus guanidine which is found to be as strongly basic in acetic acid (9) (pK', + 3.10) as dibutylamine cannot be converted to nitroguanidine by treatment of its nitrate salt with acetic anhydride–acetic acid mixtures. On the other hand the weakly basic urea (pK', − 0.93) is easily converted to nitrourea when its nitrate salt is treated with this mixture.

Chemical similarity between secondary aliphatic amines and amidines also appears during attempts to convert azo-*bis*-formamidine dinitrate (I) to azo-*bis*-nitroformamidine (III) in acetic anhydride – acetic acid mixture with or without excess of nitric acid. The yellow salt (I) is unchanged by this treatment and can be recovered. The basic strength of azo-*bis*-formamidine has not been determined because the amine is unstable, but presumably it is high. Inertness of a secondary aliphatic amine toward nitration under these circumstances would be compensated by addition of a chloride. However when acetyl chloride is included in the reaction mixture with azo-*bis*-formamidine dinitrate only the dinitrate can be recovered, and no nitro compound is formed.

The latter result is not unexpected, since guanidine nitrate is not converted to nitroguanidine in acetic anhydride containing equivalents of acetyl chloride and extra nitric acid. Since the unchanged nitrate salt is also recoverable in this case it is evident that hypochlorination of these amidines is not taking place in the anhydrous medium.

When certain secondary aliphatic amines are difficult to nitrate in presence of chloride catalyst it is advisable to convert them to the corresponding chloramines (13) which are more amenable to nitration. This cannot be accomplished in the case of guanidine since chloroguanidine is unknown. Indeed the method which was once purported to yield this chloro compound (11) has

been shown instead to be a practical synthesis of azo-*bis*-chloroformamidine (II) (17).

Azo-*bis*-chloroformamidine (II) has also been prepared from azo-*bis*-formamidine sulphate (14) and we have obtained a lesser yield from the nitrate salt (I). On the basis of its meager solubility in alkali the substance does not behave like a primary chloramine, and Structure II seems to be an adequate representation of its properties. If amidines were to behave analogously with aliphatic secondary amines then it should be possible to convert azo-*bis*-chloroformamidine (II) to the nitro analogue.

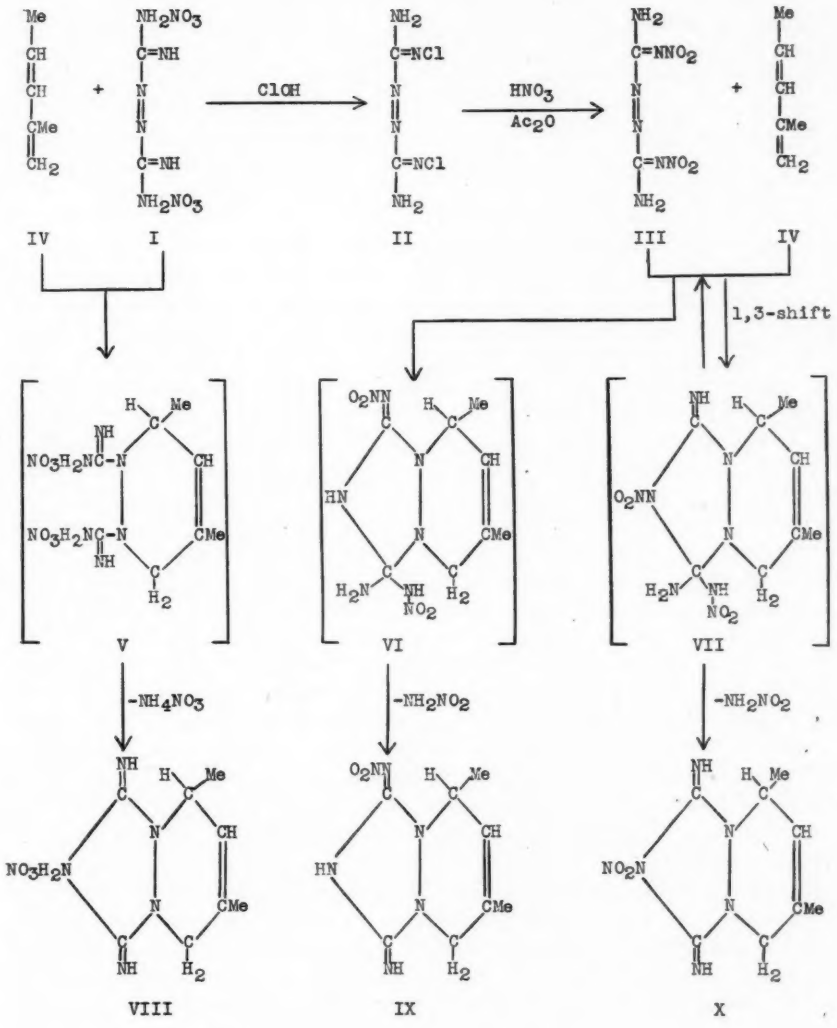
When II is treated at $-15°$ (to avoid violent decomposition at higher temperatures) with acetic anhydride and nitric acid the color of the suspension changes from yellow to red. According to elemental analysis the product is azo-*bis*-nitroformamidine (III). The low yield is not unexpected in consideration of much decomposition during the reaction.

The nitro compound III has shown no tendency to decompose after four years at room temperature. When purified by crystallization from nitromethane it gives a negative Franchimont test with diethylaniline and dissolves without decomposition in sulphuric acid or acetyl chloride. It reacts with diazomethane to give a strong evolution of gas. When heated to 165° it decomposes explosively, although it does not detonate. Massive crystals are red in color, but the flakes obtained by quick crystallizations are orange-yellow. The compound is very slightly soluble in water but it dissolves in cold alkali and is entirely recovered upon acidification. Potentiometric titration of the freshly prepared alkaline solution shows that it is a bifunctional acid with K_{A_1} about 5×10^{-6} and K_{A_2} about 5×10^{-8}.

When a substance such as nitroguanidine or 2-nitriminoimidazolidine-2 is shown by treatment with alkali initially to be nonacidic, assignment of a nitrimine structure is justified by this fact. It does not follow that those substances such as 1-nitro-2-nitramino-Δ^2-imidazoline, which react immediately with alkali to form salts, are always primary nitramines. In the latter circumstance the tautomerism may occur over seconds rather than hours. Other proofs are necessary, and 1-nitro-2-nitramino-Δ^2-imidazoline was assigned the primary nitramino structure largely because it gives a positive Franchimont test and is relatively unstable toward mineral acids (2).

The designation of structure for azo-*bis*-nitroformamidine is also not simple. The compound dissolves easily in alkali, is not very stable in concentrated sulphuric acid, and reacts vigorously with diazomethane. These properties would indicate that it was a primary nitramine. On the other hand it gives a negative Franchimont test with diethylaniline. Furthermore its reaction with 2-methylpentadiene-1,3 also favors the nitrimine structure, and the latter (III) is designated tentatively.

The reaction of III with 2-methylpentadiene (IV), which is a Diels–Alder type of addition (7), occurs smoothly in methanol or ethanol. The elementary analysis shows that the elements of nitramide have been lost in the process.


ClOH
HNO3
Ac2O
1,3-shift
-NH4NO3
-NH2NO2
-NH2NO2
IV
I
II
III
IV
V
VI
VII
VIII
IX
X

If either or both of the nitro groups had been attached to primary amino groups then intramolecular addition might be expected to occur to form VII. Alternative mutual addition of two ketimino groups is less probable, firstly because of the relative acidity of the nitramino versus the ketimino group and secondly because of steric limitations in the cyclic structure. Since nitramide might be expected to split from this ephemeral intermediate as H– and $NHNO_2$ (not, according to experience, as NO_2- and $-NH_2$) the resulting product would have the structure shown as X. Although such a compound would not be alkali-soluble, the product of the addition reaction will dissolve slowly in 5% aqueous alkali and can be reprecipitated by addition of mineral acid. The structure X would thus seem to be excluded.

On the other hand the addition of an amino group to the nitrimino group originally existent in 2,5-dinitroazo-*bis*-formamidine (III) would lead to the ephemeral intermediate (VI) from which the elements of nitramide would split to form 1-imino-3-nitrimino-4,6(or 5,7)-dimethyl-2,8,9-triaza-4,6,8,9-tetrahydroindandione-1,3 (IX). The nitrimino function has been assigned to this compound because it does not react with 0.1 normal aqueous alkali over 24 hr. Only under the conditions for actual solution (3-5% aqueous alkali) with subsequent delay of eight hours does the substance behave as a monobasic acid ($K_A = 4 \times 10^{-6}$) of approximately the expected molecular weight. Acidification of the aged alkaline solution yields 80% of IX unchanged.

The reaction comprising the elimination of nitramide subsequent to the Diels–Alder type of addition which has just been described has its counterpart in the addition of azo-*bis*-formamidine (introduced as the dinitrate (I) in presence of pyridine) to methylpentadiene (IV). The addition product (V) loses the elements of ammonium nitrate during its isolation subsequent to the Diels–Alder reaction and the actual product, according to elemental analysis, is the mononitrate* of 1,3-diimino-4,6-dimethyl-2,8,9-triaza-4,6,8,9-tetrahydroindandione-1,3 (VIII). It has not yet been found possible to convert this salt to IX either with nitric acid, nitric acid – acetic anhydride or nitric – sulphuric acids. It decomposes in these media and also decomposes when it is treated with aqueous hypochlorous acid.

This research suggests that nitration of a guanidine type occurs at the imino group rather than the primary amino group, if the position of the substituent is indicative of the position of initial attachment. Furthermore the nitration resembles that of the aliphatic secondary amines in the sense that azo-*bis*-formamidine dinitrate, which cannot be converted directly to the nitramine in acetic anhydride and nitric acid, is convertible in aqueous solution to the dichloramine which then can be converted to the dinitrimine by the nitrating mixture.

EXPERIMENTAL**

Azo-bis-chloroformamidine (II)

A suspension remained after 12.0 gm. (0.05 mole) of azo-*bis*-formamidine

*The allocation of salt linkages in the illustrated structures has been simplified for clarity in representation and does not describe the true (and unknown) structure of the salt.

**All melting points corrected against known standards.

dinitrate (16) was added to 160 ml. (0.1 mole) of cold 2.5% aqueous sodium hydroxide solution. The suspension was maintained at + 5° while 188 ml. (0.1 mole) of aqueous hypochlorous acid solution (2.9%) was added over 90 min. After a subsequent 90 min. period at the same temperature the whole was filtered and washed with ethanol and ether. The yield of product melting at 149° weighed 4.0 gm. This 44% yield was purified (50% recovery) from 500 ml. of boiling water, m.p. 152°, or from boiling dioxane (5 cc. per gm.), m.p. 157-158° (decomp.). Despite a report (14) of two polymorphic forms we were only able to isolate one. However, the crystals appeared pseudomorphic when isolated from dioxane, so an unstable polymorph may have been present during crystallization. A mixed melting point with an authentic sample was not lowered. The compound reacted vigorously with etherous diazomethane, but did not dissolve in dilute alkali.

The X-ray diffraction pattern spacings (*Kx*) using CuK_α radiation (Ni filtered) at relative intensities $[I/I_0]$ is [10] 4.18; [8] 3.47; [3] 2.66, 2.03, 1.90; [2] 3.09, 2.95, 2.25, 2.13, 1.75; [1] 6.69, 5.14, 4.47, 2.88, 1.62; [0.5] 3.76, 3.27, 1.84, 1.81, 1.47; [0.4] 1.52; [0.3] 1.69, 1.64, 1.57.

Azo-bis-nitroformamidine (*III*)

Acetic anhydride (0.5 mole, 48 ml.) was stirred at −15° while one-eighth of 7.1 ml. (0.17 mole) of 98.8% nitric acid was added at the beginning of each 10 min. period, during which time interval one-eighth of 14.6 gm. (0.08 mole) of azo-*bis*-chloroformamidine was added. The 80 min. addition period permitted a reaction temperature of −11° to −13° except at the end where it increased to −5° with a corresponding increase in gas evolution. The unstable reaction mixture was then poured at once into ice, and 10 gm. of sodium bisulphite was immediately stirred in. When solution of this salt was complete the nitro compound was filtered off, water-washed, and vacuum-dried at 50°. The weight (4.7 gm.) represents 29% of theoretical yield. The yield was doubled when the size of experiment was reduced to 5% of the quantities described above. The recovery from 4.7 gm. after crystallization from boiling nitromethane (57 ml. per gm.) was 3.20 gm. The compound gave a reddish color rather than the characteristic green in the Franchimont test with dimethyl- or diethylaniline.

Anal. Calcd. for $C_2H_4N_8O_4$: C, 11.78; H, 1.97; N, 54.8. Found: C, 11.8; H, 2.00; N, 54.5.

In absence of a satisfactory melting point the X-ray diffraction powder pattern was determined (CuK_α, Ni filter) in *Kx* spacings at relative intensities $[I/I_0]$ as [10] 2.86; [6] 3.22; [5] 3.97; [4] 4.86; [3] 4.14, 3.44; [2] 1.69, 1.62; [1] 5.20, 2.77, 2.39, 2.09; [0.5] 2.66, 2.45, 2.31, 2.24, 2.20, 2.15, 2.04, 1.61, 1.59; [0.3] 1.90, 1.85; [0.2] 1.55.

Potentiometric titration of a cold freshly prepared alkaline solution (agitated by a nitrogen stream) containing 0.1000 gm. of nitro compound, 173.7×10^{-5} mole of alkali and 30 ml. of water with $\frac{N}{10}$ hydrochloric acid gave an apparent

molecular weight of 206 (calcd. 204) if the substance were a dibasic acid (K_{A_1} and K_{A_2} are about 10^{-6} and 10^{-8} respectively). The color intensity of the nitromethane extract of the acidified solution increased over several hours. Azo-*bis*-nitroformamidine reacted readily with etherous diazomethane and was decomposed by concentrated sulphuric acid. Both reagents caused gas evolution.

When azo-*bis*-formamidine dinitrate (I) was treated under similar nitration conditions with or without the inclusion of acetyl chloride no evidence of nitration was observed. The color of the suspension did not change and the nitrate salt (I) could be recovered. Solution of I in concentrated sulphuric acid did not cause decomposition. Dilution of this solution after two hours reprecipitated the salt.

1-Imino-3-nitrimino-4,6(or 5,7)-dimethyl-2,8,9-triaza-4,6,8,9-tetrahydroindane

A suspension of 2.04 gm. (0.01 mole) of azo-*bis*-nitroformamidine (III) in 25 ml. of absolute methanol was treated with 3.28 gm. (0.04 mole) of 2-methylpentadiene-1,3. The stirred reaction mixture became warm in 15 min. Within an hour the solid had dissolved completely and the solution was colorless. The reaction mixture was allowed to stand until crystallization was complete. The colorless crystal crop weighed 1.17 gm., m.p. 254-256°. The gummy mass remaining after evaporation of the methanol was treated with 5% alkali and ether and the separated, chilled alkaline layer was acidified with acetic acid. An additional 0.26 gm., m.p. 245-246° raised the total yield to 1.43 gm. or 65% of theoretical. The whole was recovered in 65% yield, m.p. 258.5-260.6°, after crystallization from boiling methanol (60 ml. per gm.). A lower yield of product (43%) was obtained when ethanol was used as the reaction medium, and by-product formation was evident. Calc. for $C_8H_{12}N_6O_2$: C, 42.8; H, 5.42; N, 37.5%. Found: C, 42.7; H, 5.20; N, 38.0%. The compound gave a negative Franchimont test with dimethyl aniline. It was recovered unchanged when heated for 10 min. with a 1:1 mixture of acetic acid and acetyl chloride.

A solution of 0.1110 gm. (5×10^{-4} mole) of the compound in 4 ml. methanol and 35 ml. water was supersaturated but could be titrated with acid after addition of 15 ml. 0.1 *N* alkali. A solution of 0.1110 gm. in 1 ml. 10% aqueous sodium hydroxide and 2 ml. of methanol was stable at + 5° for 24 hr. and then could be diluted with 35 ml. water and titrated potentiometrically with acid without apparent precipitation. In both cases the titration indicated only the hydrochloric acid. Alternatively a suspension of 0.1110 gm. was aged in 10 ml. of 10% aqueous sodium hydroxide for 10 hr., then diluted to 45 ml. and aged for eight hours at 25°. It was then chilled and neutralized with 10% hydrochloric acid to pH 11.3. Subsequent titration with 0.1 *N* acid gave two inflections for a monobasic acid of molecular weight 218 (calcd. 222). The midpoint of this inflected curve was found at pH 6.4 on the Coleman pH meter. Evaporation of the acidified solution yielded 80% of the original substance, m.p. 259-260°.

1,3-Diimino-4,6-dimethyl-2,8,9-triaza-4,6,8,9-tetrahydroindandione-1,3-mononitrate (VIII)

When a stirred yellow suspension of 4.80 gm. (0.02 mole) of azo-*bis*-formamidine dinitrate in 50 ml. of anhydrous methanol was treated with 32 ml. (0.04 mole) of anhydrous pyridine the solid and reaction medium became red. To this stirred solution was added 1.64 gm. (0.02 mole) of freshly distilled 2-methylpentadiene-1,3. After six days the color had disappeared. The filtered reaction mixture was evaporated *in vacuo* and the residue washed with ether and then dissolved in 10 ml. of boiling methanol. The chilled solution was diluted with 5 ml. of ethanol and 1.40 gm., m.p. 193-194°, was filtered off. This 29% yield could be augmented by 0.63 gm., m.p. 191-192°, when the filtrate was cautiously diluted with ether, but further dilution yielded 1.44 gm. of impure ammonium nitrate, m.p. 155-165°. Crystallization of the crude organic reaction product from boiling water (7 ml. per gm.) raised the melting point to 194-195°. Subsequent crystallization from boiling ethanol (8 ml. per gm.) brought the melting point to constant, 196.5-196.8°.

Anal. Calcd. for $C_8H_{14}N_6O_3$: C, 39.7; H, 5.81; N, 34.7. Found: C, 39.8; H, 5.99; N, 34.7.

When an aqueous solution was treated with picric acid a picrate was precipitated in good yield. It melted at 253.5-254.2° after having been washed with ethanol and ether.

Anal. Calcd. for $C_{14}H_{16}N_8O_7$: C, 41.2; H, 3.94; N, 27.4. Found: C, 41.3; H, 4.10; N, 27.8.

When VIII was treated with nitric acid, nitric acid – acetic anhydride, or nitric – sulphuric acid mixtures a deep red color appeared and gas was evolved slowly if the temperature were allowed to rise about 10°. The negligible amount of product obtained from these experiments was noncrystalline and did not possess the properties of IX. An attempt to obtain the chloramine corresponding to VIII with aqueous hypochlorous acid likewise led to considerable gas evolution but negligible product.

Nitrourea

A suspension of 1.23 gm. (0.01 mole) of urea nitrate in 2.42 ml. (0.025 mole) of acetic anhydride and 2.5 ml. of acetic anhydride was stirred for one day. The medium was then removed by distillation under 15 mm. pressure. To the residue was added 4 ml. of water at 2°C. The undissolved solid was filtered off, wt. 0.45 gm., m.p. 142° (decomp.). This substance (43% yield) gave a strong green Franchimont test with diethylaniline. Its X-ray diffraction powder pattern (CuK_α radiation, Ni filtered) was found to be identical with that of nitrourea by comparison of spacings (*A*) at relative intensities [I/I_0]: [10] 3.21; [8] 3.31; [7] 3.68; [5] 2.49; [4] 4.72, 4.21, 3.08; [3] 4.48; [2] 2.75, 2.67; [1] 3.46.

Guanidine Nitrate with Acetic Anhydride

The preparation of nitrourea was duplicated exactly except that 1.22 gm. (0.01 mole) of pure guanidine nitrate was used instead of the urea salt. Only

guanidine nitrate and no nitroguanidine was found in the residue. When guanidine nitrate was treated with a five-fold molar excess of acetic anhydride either at room temperature for nine days or for six hours at 65°-70° the salt was recovered unchanged. It was also recovered unchanged when 1.22 gm. (0.01 mole) was treated with 4.85 ml. (0.05 mole) of acetic anhydride and 0.43 ml. (0.01 mole) of absolute nitric acid, initially at − 40°C. and finally at 25° for three hours, whether or not an extra equivalent of nitric acid and acetyl chloride was included. On the other hand 1.22 gm. of this guanidine nitrate reacted with 5 ml. of 95% sulphuric acid during two hours to give a 46% yield of nitroguanidine.

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NOTES

A New Synthesis of Piperidine

Piperidine is produced commercially in limited quantities by the catalytic hydrogenation of pyridine obtained from coal-tar. In view of the very small percentage of pyridine in this source, 0.1%, and the necessity of a careful purification to prevent catalyst poisoning in the hydrogenation reaction, a new process for the production of either piperidine or pyridine based on some other readily available starting material would have considerable value. It may be pointed out that piperidine can be readily converted into pyridine; therefore a method for the production of the former might at the same time serve to supplement coal-tar as a source of pyridine.

A promising intermediate for the synthesis of piperidine is the compound tetrahydropyran which may be produced from readily available furfural. The direct conversion of tetrahydropyran to piperidine by the vapor-phase reaction with ammonia over alumina has been studied by Yur'ev (5) and by Kline and Turkevich (4). Yields of the secondary amine did not exceed 20%. Recent work in the authors' laboratory (1) has demonstrated that tetrahydropyran may be converted to N-phenylpiperidine in over 90% yield by reaction with aniline over alumina. This has suggested an indirect route for the synthesis of piperidine from the cyclic ether, since N-phenylpiperidine, a tertiary aromatic amine, should be capable of nitrosation to N-(*p*-nitrosophenyl)-piperidine and this, in turn, of conversion into piperidine and *p*-nitrosophenol by hydrolytic cleavage with alkali.

Le Fèvre (3) attempted to nitrosate N-phenylpiperidine but was unsuccessful. Bradley (2) obtained N-(*p*-acetaminophenyl)-piperidine by nitrosation of N-phenylpiperidine followed by zinc dust reduction and acetylation. He did not attempt to isolate the intermediate nitroso compound. Hydrolysis of the nitrophenylpiperidines has been studied by Le Fèvre (3). He found that whereas picrylpiperidine readily produced piperidine on brief boiling with 2*N* sodium hydroxide, the mono and dinitro compounds failed to yield the secondary amine in a detectable quantity even after prolonged boiling with alkali.

We have found that N-phenylpiperidine may be nitrosated satisfactorily using sodium nitrite and hydrochloric acid, and that the resulting N-(*p*-nitrosophenyl)-piperidine hydrochloride may be hydrolyzed by heating with excess aqueous sodium hydroxide to give piperidine in an over-all yield of 65-70%. A careful study has been made of both the nitrosation and hydrolysis reactions and, from the results obtained, it is possible to draw the following conclusions.

Nitrosation Reaction

1. The reaction temperature is not critical although 3-5°C. would appear to be optimum.

2. Only a very slight excess of sodium nitrite is required; maximum yields are obtained using 1.01 moles of 99.5% sodium nitrite per mole of N-phenylpiperidine. A larger excess of sodium nitrite gives a greater yield of the crude nitroso compound but the product is less pure and the over-all yield of piperidine is not improved.
3. Best results are obtained using a 10% excess of hydrochloric acid, that is, a total of 2.20 moles per mole of N-phenylpiperidine.
4. A concentrated reaction mixture is desirable. This necessitates the use of a saturated solution of sodium nitrite and concentrated (12*N*) hydrochloric acid. A considerable reduction in yield is obtained when more dilute solutions are employed.

Hydrolysis Reaction

1. Either crude solid N-(*p*-nitrosophenyl)-piperidine hydrochloride or the entire nitrosation reaction mixture may be employed. Better over-all yields of piperidine, however, are obtained using the latter.
2. The amount and concentration of alkali are not critical. Maximum yields result, however, when the hydrochloride salt is treated with an approximately 0.6 *N* solution of sodium hydroxide of sufficient volume to provide four to six moles of base per mole of salt.
3. The hydrolysis reaction mixture may be refluxed for 7 to 10 hr. and the piperidine obtained as a dilute aqueous solution by steam distillation. A more satisfactory method is to attach the reaction flask, after addition of the alkali, to an efficient fractionation column and to heat the mixture at total reflux for a period of one-half hour. A distillate boiling at 92-95°C. and consisting of a piperidine–water azeotropic mixture (65% piperidine by weight) is then collected slowly.

EXPERIMENTAL

Nitrosation of N-Phenylpiperidine

To a solution of 30.0 gm. (0.200 mole) of N-phenylpiperidine in 12 *N* hydrochloric acid (0.440 mole) was added 13.9 gm. (0.202 mole) of sodium nitrite dissolved in 18 ml. of water. The addition, conducted with constant stirring in a nitrogen atmosphere at 3-5°C., required 45 min. After stirring for an additional 30 min. the solid N-(*p*-nitrosophenyl)-piperidine hydrochloride was separated by filtration; yield, 30-33 gm. or 70-75%. Purification was effected by conversion of the hydrochloride to the free base with alkali, crystallization of the base from isopropanol, reprecipitation of the salt by passing anhydrous hydrogen chloride into an ether solution of the base, and a final crystallization of the salt from methanol. The pure hydrochloride consisted of lemon-yellow crystals which exhibited no definite melting point. Calc. for $C_{11}H_{15}N_2OCl$: C, 58.28; H, 6.67; N, 12.36; Cl, 15.64%. Found: C, 59.22, 59.44; H, 7.05, 7.03; N, 12.53, 12.64; Cl, 15.01, 14.99%.

The free base crystallized from isopropanol as bright green plates; m.p. 53.5-54.0°C. Calc. for $C_{11}H_{14}N_2O$: C, 69.44; H, 7.42; N, 14.73%. Found: C, 70.04, 69.97; H, 7.46, 7.63; N, 14.24, 14.31%.

For further identification, the hydrochloride salt was converted to N-(*p*-acetaminophenyl)-piperidine by reduction with zinc dust in hydrochloric acid followed by acetylation of the resulting *p*-amino compound with acetic anhydride and sodium acetate; m.p. 151.6-152.7°C. Bradley (2) reports 151-152°C. for this compound.

Hydrolysis of N-(p-Nitrosophenyl)-piperidine

The entire nitrosation reaction mixture obtained from the nitrosation of 30.0 gm. (0.200 mole) of N-phenylpiperidine was transferred to a 2-liter flask and 33.6 gm. (0.840 mole) of sodium hydroxide dissolved in 1300 ml. of water added. The flask was attached to a 20-plate Fenske column and heated under total reflux for 30 min. A distillate boiling at 92-95°C., the piperidine-water azeotrope, was then collected slowly. The over-all yield of piperidine, obtained as a 60-65% by weight aqueous solution, was 65-70% based on N-phenylpiperidine. When the crude solid hydrochloride was used in the hydrolysis reaction, the yield based on the salt was 75-80% and the over-all yield 52-57%.

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The Isotopic Constitution of Igneous Sulphur and the Primordial Abundance of the Terrestrial Sulphur Isotopes

In view of the large variations that have been found in the abundance of the sulphur isotopes in naturally occurring compounds (1-6), it seemed important to determine the original abundance of the sulphur isotopes prior to any biological or geological fractionation processes occurring on the earth's surface.

It has been suggested (2) that the isotopes of meteoritic sulphur have not been subjected to these fractionation processes and, therefore, their abundance should be considered as a base level from which all isotopic fractionation has occurred for terrestrial sulphur. Since sulphur of igneous origin is probably the nearest that man will come to securing terrestrial sulphur which has been unaltered isotopically following the formation of the earth's crust, igneous sulphur samples were collected and their S^{34} content compared with meteoritic sulphur.

The igneous sulphur samples were obtained both from igneous rocks and sulphide ores of igneous origin. During the early stages of crystallization of the earth's molten magma (around 1000°C.), sulphur is distributed between a

sulphide melt and a silicate melt (igneous rocks) which are only partially miscible. The sulphides pyrrhotite, pentlandite, and chalcopyrite in the sulphide melt are classified as sulphides of igneous origin and are sometimes referred to as ultrabasic intrusions of sulphide. When the magma has reached the granitic stage of cooling, 500-600°C., further sulphide ores of igneous origin crystallize out in hydrothermal veins. However, the total sulphur content of the ultrabasic intrusions and the hydrothermal veins constitute a negligible percentage of the total igneous sulphur. Most of the sulphur remains as a sulphide in the igneous rock.

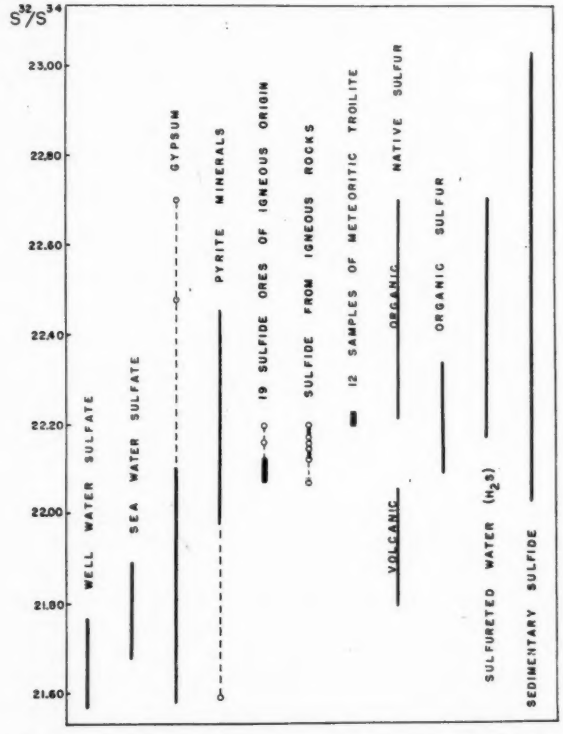

FIG. 1. Distribution of S^{34} in terrestrial and meteoritic sulphur.

The sulphur samples were converted to sulphur dioxide and their relative S^{34} concentrations determined with a 180 degree Nier type mass spectrometer by comparing each sample with a standard (Park City pyrite) in a manner described previously (5). The S^{32}/S^{34} ratios of the igneous sulphur samples may be compared directly with our previous results since oxygen of the same isotopic composition was used in preparing all the sulphur dioxide samples. The results are shown in Table I and illustrated graphically in Fig. 1.

It is seen from Fig. 1 that the isotopic composition of igneous sulphur is

TABLE I

SULPHUR ABUNDANCE DATA FOR SULPHIDE SAMPLES OF IGNEOUS ORIGIN

Sample	Location	S^{32}/S^{34} ratio
Igneous rocks		
Norite	Stillwater Complex, Montana	22.08 ± 0.01*
Lava	Paricutin Volcano, Mexico	22.13 "
Syenite	Otto Twp., Ont.	22.16 "
Norite	Murray Mine, Sudbury, Ont.	22.17 "
Nipissing diabase	Hecla Mine, Cobalt, Ont.	22.18 "
Diabase	Ossion Twp., Ont.	22.21 "
Sulphide ores of igneous origin		
Pyrrhotite	Falconbridge Mine, 1400 ft. (Sudbury, Ont.)	22.11 ± 0.01*
"	" " 1700 ft. " "	22.08 "
"	" " 2800 ft. " "	22.11 "
"	McKim Mine (McKim Twp.), 1000 ft. " "	22.12 "
"	Blezard Twp., Ont. 1400 ft. " "	22.14 "
"	Levack Twp., Ont. 3000 ft. " "	22.10 "
Chalcopyrite	" " " " " " "	22.09 "
Pyrrhotite	Denison Twp. Worthington Offset " "	22.11 "
"	Bowell, Ont., Foy Offset " "	22.13 "
"	Massive sulphide " "	22.14 "
Pyrite	" " " "	22.10 "
"	" " Falconbridge " "	22.13 "
"	Lamaque, Que.	22.08 "
"	" "	22.12 "
Pyrrhotite	40 miles N.E. of Yellowknife, N.W.T.	22.08 "
Chalcopyrite in calcite vein	Nu-Silco Mine, Timiskaming, Ont.	22.12 "
Sulphide from hydrothermal vein in Nipissing diabase	Hecla Mine, Cobalt, Ont.	22.14 "
Chalcopyrite	Stillwater Complex, Montana	22.21 "
Pyrrhotite	" " "	22.17 "

* *Average error.*

constant within 0.5% and that the S^{32}/S^{34} ratios agree more closely with the value found for meteoritic sulphur than that of the sulphur in any other group. Since the sulphur in igneous rocks accounts for the greater part of igneous sulphur one might expect that its S^{34} content would remain essentially unchanged from the primordial abundance and probably have an isotopic abundance very nearly the same as that of meteoritic sulphur. Of the six samples investigated, the isotopic ratios of five of them agree within 0.2% and the values overlap with those for meteoritic sulphur. The close agreement between the S^{32}/S^{34} ratios for the sulphur in igneous rocks and meteorites is further evidence in favor of the theory that meteorites and the earth were formed from a common origin. In this connection Urey has found that the isotopic composition of igneous and meteoritic oxygen is identical (7).

On the other hand, the sulphide ores of igneous origin which constitute a negligible portion of the igneous sulphur should reveal any isotopic fractionation that occurred as the sulphide minerals crystallized from the magma. Although the S^{32}/S^{34} ratios of the igneous rocks and the sulphide ores of igneous origin (Fig. 1) overlap somewhat, the majority of the sulphide ores appear to be enriched by 0.5% in S^{34} with respect to meteoritic sulphur. Thus some

fractionation of the sulphur isotopes would seem to occur as a result of early fractional crystallization of sulphide minerals.

The isotopic uniformity of the sulphide deposits in the Sudbury district (Table I) is quite interesting and may possibly prove to be of great practical importance to the geologists in determining the origin of the offset and marginal deposits of the world famous "nickel eruptive" in that area.

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A Note on the Thermodynamic Properties of the Hydrates of Sodium Carbonate

In the course of work done at this laboratory we have calculated the values of the heat and free energy of formation and of the entropy of the three hydrates of sodium carbonate. These values, which have not been reported previously, are given in Table I. The standard state of carbon has been assumed to be β-graphite.

TABLE I

HEAT OF FORMATION, FREE ENERGY OF FORMATION, AND ENTROPY OF SODIUM CARBONATE AND ITS HYDRATES AT 25°C.

	$\Delta H°$ cal.	$\Delta F°$, cal.	$S°$, cal./degree
Na_2CO_3	−271,020	−251,110	32.5
$Na_2CO_3.H_2O$	−342,720	−308,640	40.7
$Na_2CO_3.7H_2O$	−765,620	−647,890	94.5
$Na_2CO_3.10H_2O$	−975,980	−818,430	128.2

The data for the anhydrous sodium carbonate have been taken from the compilation of Kelley and Anderson (6). The other heats of formation are based on this value and on the heats of solution of the four salts reported by Bichowsky and Rossini (2). The heats of dissociation of the monohydrate and of the decahydrate calculated from the dissociation pressure measurements

of Caven and Sand (3, 7) and of Baxter and Cooper (1, 7) are in good agreement with the values derived from the heats of solution (2), and the heat of vaporization of water (10).

The free energy of formation of the monohydrate was calculated from the value for the anhydrous salt (6) and the dissociation pressure as measured by Caven and Sand (3, 7). The free energy of formation of the decahydrate was calculated from solubility data, viz.: the solubility of sodium carbonate decahydrate (7); the vapor pressure of pure water (10); the vapor pressure of the saturated solution (7); the free energies of formation of the sodium ion (8), of the carbonate ion (6, 9), and of water (10); and the activity coefficient of sodium carbonate in the saturated solution. As this last datum is not known, the value of the activity coefficient of potassium carbonate in a solution of the same concentration (8) was used. Fortunately even a relatively large error in this value has only a small influence on the final result. The method of calculation was similar to that used by Johnston and Bauer (4) for $LiOH.H_2O$. The free energy of formation of the heptahydrate was calculated from the value of the decahydrate in conjunction with the dissociation pressure measurements of Baxter and Cooper (1, 7).

The entropy of formation was calculated from the relation

$$T\Delta S = \Delta H - \Delta F$$

and the absolute entropy of the salt was derived from this value and the entropies of the elements reported by Kelley (5).

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